The Synthesis and Thermal Rearrangement of 2,5-Dialkyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol's

by

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Doctor of Philosophy
in
Chemistry

Approved

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J. Wightman

J. Wolfe

May, 1985
Blacksburg, Virginia

Dedication

In some ways it was very difficult to decide how to dedicate this work. The person I am now exists because of everyone and everything that I have come in contact with. The people of my hometown will always have a very special place in my heart, no matter where I am. I'll always remember how hard we had to work to make a living and how our faith always saw us through.

There have been other special people in my life. The one who has really helped me to become more positive in my attitudes and my confidence is the only one that I can really dedicate this work to. Over the past 4 years, has helped me to become a stronger person and hopefully a better chemist. So with all due respect to the others, I dedicate this work to my wife,

Acknowledgements

I would like to thank my research group (Robert, Pat, Bill, Alan, Mike, and especially Dr. Ogliaruso) for the help and friendship I have benefited from during the past years.

I am grateful to Dr.'s Bell, Mason, Wightman, and Wolfe for donating their time to serve on my committee.

I would like to thank Dr. McNair and his research group (especially Jeff, Mike, and Jack) for their help with the "Blue Monster."

I would like to acknowledge the help that my family has given me. No matter what the problem, Mom, Dad, , , and were always there for me.

Thanks to all of my special friends (Jay, Leigh, Jr., Vicie, Phil, Dan, Lenwood, Dwight, BJ, Roger, Robert, and Mike) for the support you gave me during my college years. We shared a lot of friendship and heartache, but it helped us grow up. Together we made it.

I would like to thank , , and those people at the American Red Cross, Bethesada, Maryland, who assisted in the preparation of this dissertation.

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I. Introduction

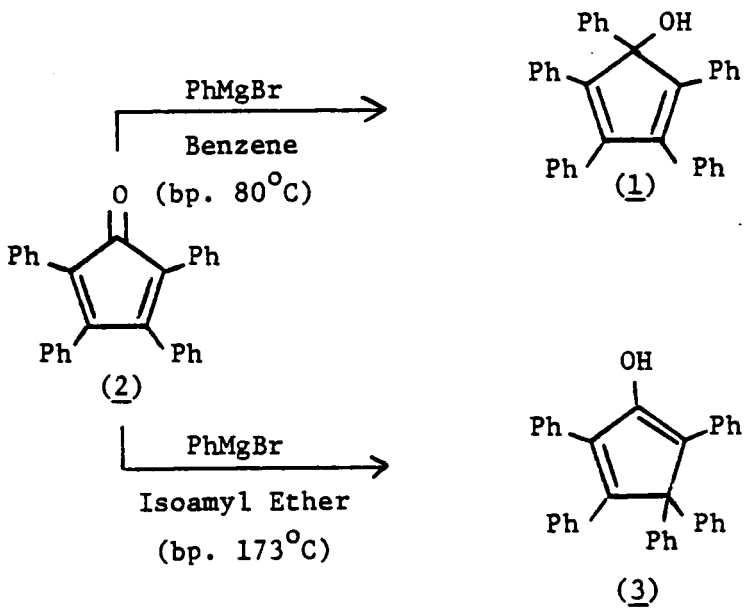
The thermally allowed suprafacial [1,5]-sigmatropic rearrangement of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol(1) has been studied extensively since its discovery. Although this phenomenon was explained by the Woodward and Hoffmann rules for electrocyclic reactions, some questions concerning the actual mechanism and transition state still existed. In order to answer these questions, the kinetics of the rearrangement of several derivatives of (1) have been investigated. To date these studies were confined only to aromatic derivatives of (1).

As an extension of this investigation, the current study was done on alcohols having alkyl groups at the 2- and 5- positions of the parent 5-membered ring. This study was initiated to establish if rearrangements of these types of compounds were indeed possible, to establish if the steric bulk of the alkyl groups would affect the rate of the rearrangement relative to (1), and to determine if this effect was observable throughout an alkyl series.

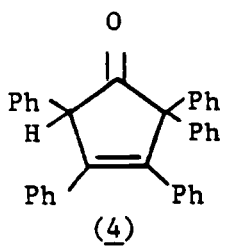
II. Historical

A. Theoretical

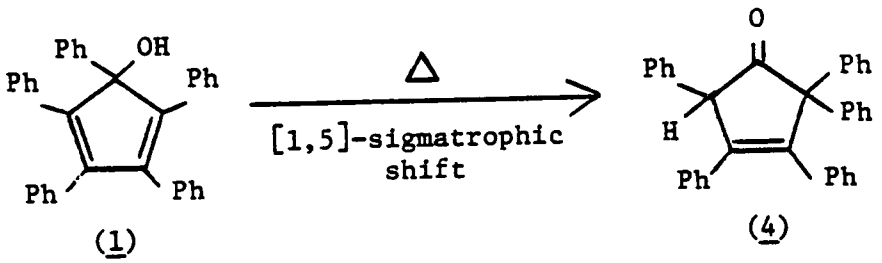
Allen and Van Allen[1] discovered that the products obtained from the reaction of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one with phenylmagnesium bromide differed, depending on the temperature used for the reaction.



When Dufraisee, et al.,[2] investigated this process, they found that the structure of (3) was incorrect and that the correct structure was actually (4).

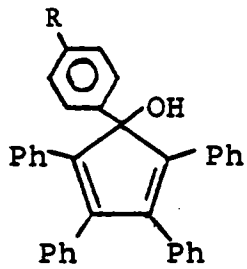


Youssef and Ogliaruso,[3] while investigating this reaction, were able to: 1) correct all structures from Allen and Van Allen's work, 2) eliminate ionic and radical involvement as possible reaction mechanisms, and 3) define this rearrangement as a thermally allowed suprafacial [1,5]-sigmatropic shift of phenyl. This conclusion was reached by applying the Woodward and Hoffmann rules for orbital symmetry.[4]



(1) (4)

Since that time studies have been done on various aspects of this rearrangement. The first studies involved the synthesis and rearrangement of derivatives of (1) in which the phenyl rings had been substituted with groups of different electronegativities. It was hoped that the kinetics of the rearrangements would show a dependence on the electronegativity of the substituent. The following series of compounds were synthesized and studied.



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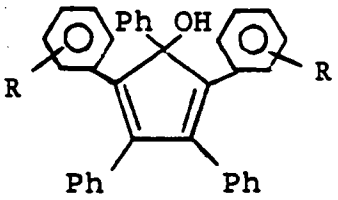

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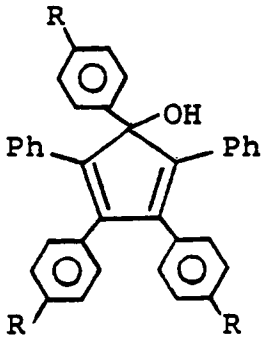
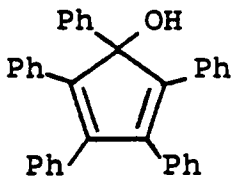


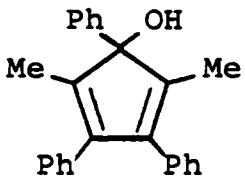
(7)

The studies indicated that regardless of whether the electronegative substitutuent was on the migrating species (5),[5] the migration terminus (6),[6] or on both the migrating species and the 3,4-phenyl rings (7),[7] there was no substantial influence on the kinetics of the rearrangement by these substituents.

For the current study it was necessary to synthesize the following alcohols: 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol(8), 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol(9), 2,5-di(t-butyl)-1,3-diphenyl-2,4-cyclopentadien-1-ol (10), 15,16,17-triphenylbicyclo-[12.2.1]heptadeca-14,16-dien-17-ol(11), and parent alcohol (1). Of these alcohols only parent alcohol (1) and (8) had been synthesized, although the structure of (8) had been mistakenly assigned as 2,5-dimethyl-3,3,4-triphenyl-1,4-cyclopentadien-1-ol (12).[8]



(1)



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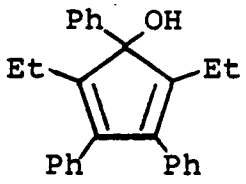

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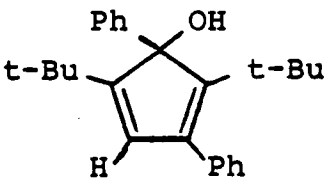

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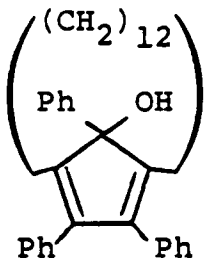

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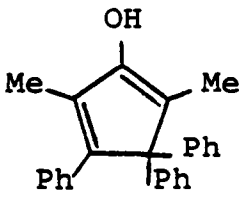
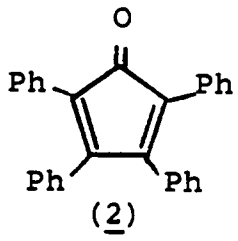


(12)

Before these alcohols could be synthesized, precursor ketones which would be used in their synthesis had to be prepared. All precursor ketones were known and were synthesized using known procedures. The precursor ketones were 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13), 2,5-diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14), 2,5-di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (15), 15,16-diphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-one (16), and tetracyclone (2).



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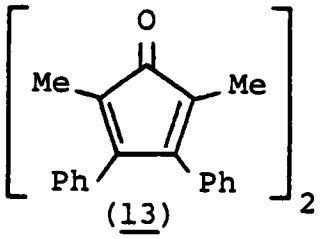

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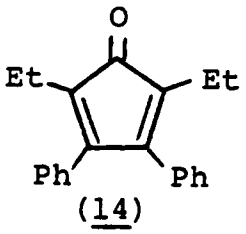

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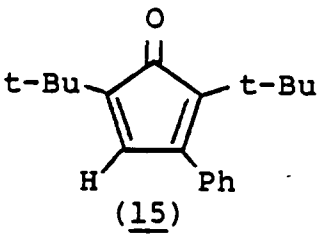

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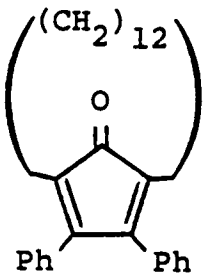


(16)

B. Synthetic

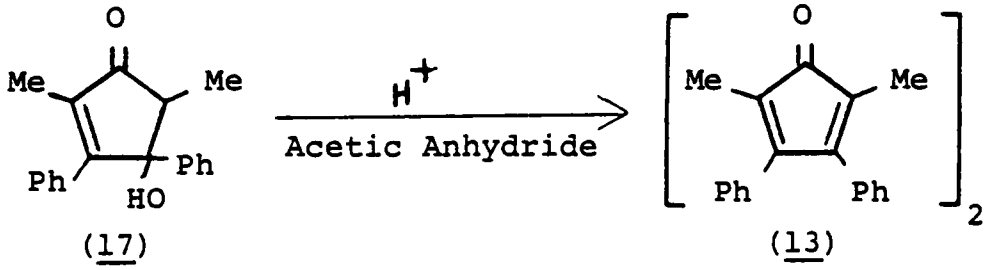
The remainder of this section will be a review of previous synthetic procedures for the preparation of the aforementioned compounds.

1. Previous synthetic methods for the preparation of precursor ketones.

a. Preparation of 2,5-Dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13).

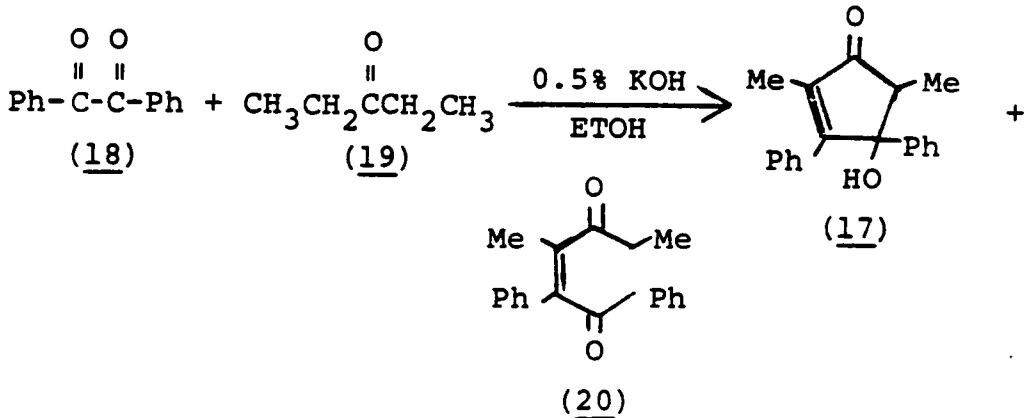
The dimer 13 was first synthesized by Gray[9] from 2,5-dimethyl-3,4-diphenyl-2-cyclopenten-3-ol-1-one (17). The dimer was formed by dehydration of 17. This was accomplished by adding a drop of sulfuric acid to a suspension of

17 in acetic anhydride. The crude product 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13) was purified by recrystallization from ethanol.



(17) (13)

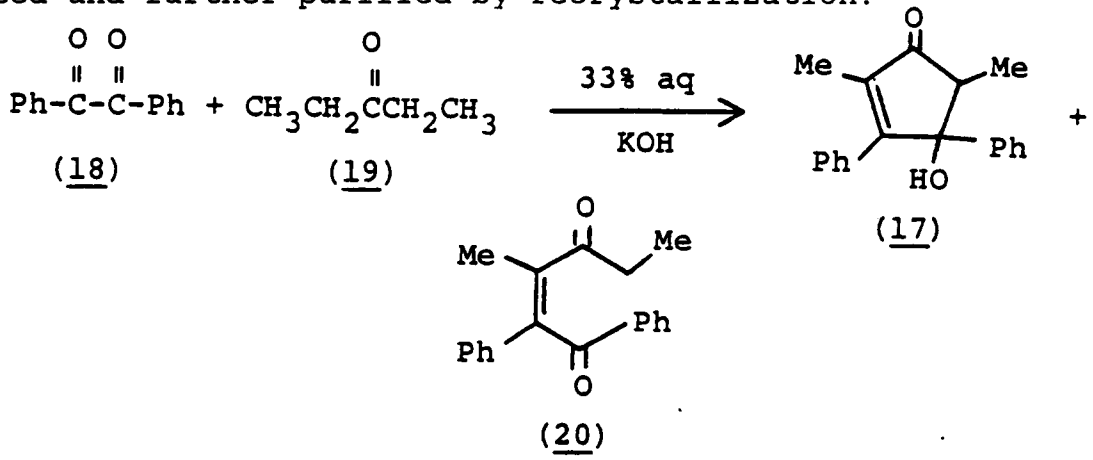
The precursor alcohol 17 was first synthesized by Japp and Meldrum[10] in two ways. The alcohol 17 was prepared by reacting benzil (18) and 3-pentanone (19) in 0.5% ethanolic potassium hydroxide for 1 month. During this time 17 and an open chain isomer 20 were formed. The two compounds were isolated by precipitation from water and purified by fractional crystalization into their pure state.



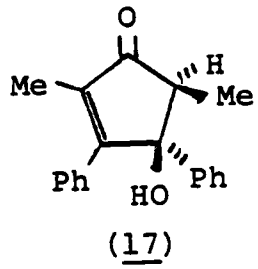
(18) (19) (17) (20)

The alcohol 17 was also prepared by reacting benzil (18) and 3-pentanone (19) in warm 33% aqueous potassium hydroxide for 24 hours. The products obtained from this

reaction were the same as those obtained from the previous procedure except 17 was produced in greater quantity than previously stated relative to 20. The products were separated and further purified by recrystallization.



Later work by Clark[11] proved that 20 was cyclic and had a diastereoisomeric relation to 17.



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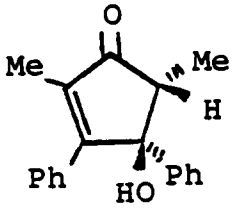


(20)

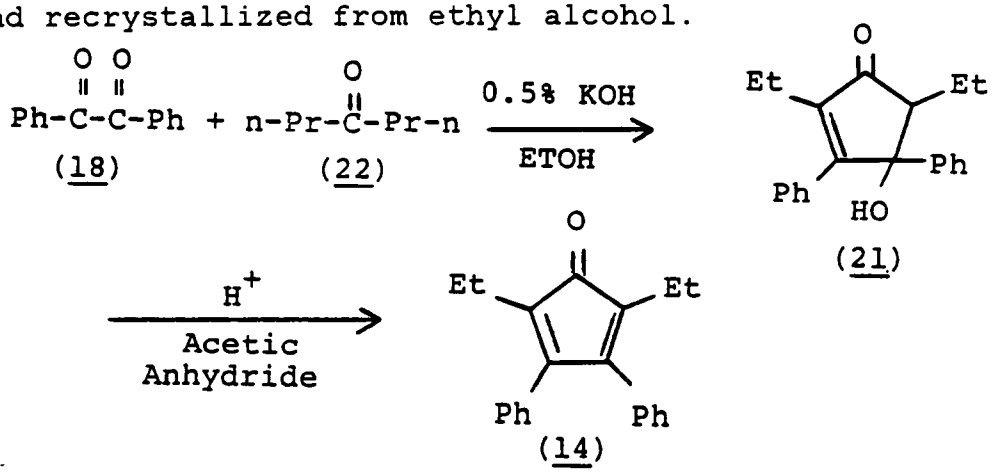
These synthesis of 17 and 20 along with their subsequent conversion to 13 provide the only known method for the preparation of 13.

b. Preparation of 2,5-Diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14).

The title compound was also formed via the dehydration of 2,5-diethyl-3,4-diphenyl-2-cyclopenten-4-ol-1-one (21) by Allen and Van Allen.[12] The alcohol 21 was prepared in the following manner. Benzil (18) and 4-heptanone (22) were reacted in 0.5% ethanolic potassium hydroxide for 48 hours. After this time the product was crystallized from water and the crude product 21 purified by recrystallization from ethyl alcohol.

Japp and Meldrum[10] made this compound using essentially the same procedure with the exception that the reaction time used was 1 month.

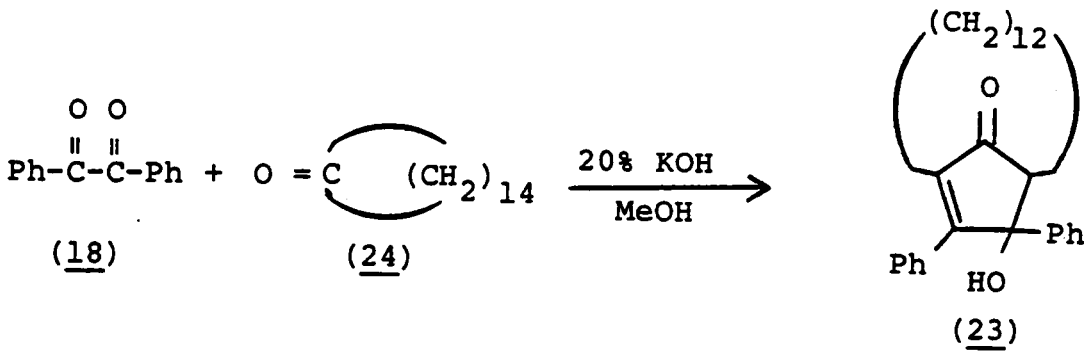
The 2,5-diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14) was prepared by dehydration of either the crude or purified alcohol 21. This was done by adding concentrated sulfuric acid to a stirred suspension of 21 in acetic anhydride. After 1 h the product 14 was crystallized from water and recrystallized from ethyl alcohol.

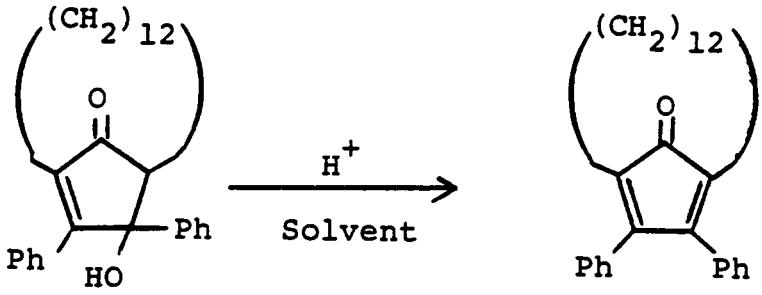


The only other known synthesis of this compound was by T. Ashida.[13] However, no specific information is known about this procedure.

c. Preparation of 15,16-Diphenylbicyclo[12.2.1]hepta-deca-14,16-dien-17-one (16).

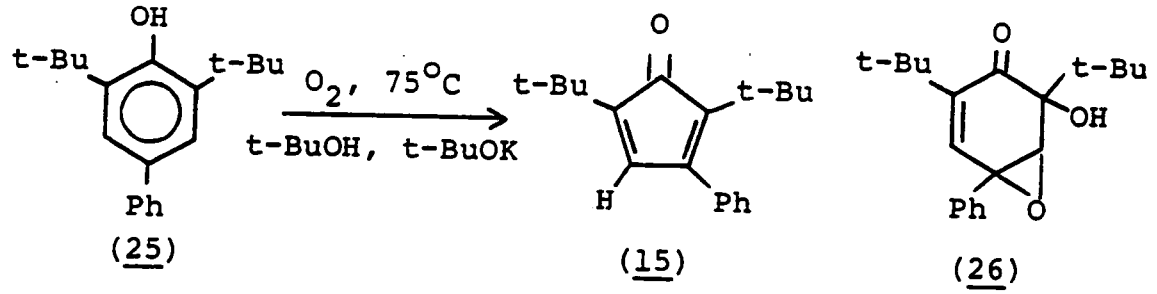
The title compound was first synthesized by Allen and Van Allen[14] via dehydration of 15,16-diphenylbicyclo [12.2.1]heptadeca-14-en-16-ol-17-one (23). The alcohol 23 was prepared by reacting benzil (18) with cyclopentadecanone (24) for 1.5 h using methanol as solvent and 20% methanolic potassium hydroxide as the base. The product from this reaction was an oil, 23, which was dehydrated to give 15,16-diphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-one (16) using any of three methods. 1). The oil 23 was dissolved in acetic anhydride, a drop of concentrated sulfuric acid added, and the stirred solution heated at 70°C for 5 min. The crude product 16 crystallized upon cooling. 2). The oil 23 was dissolved and refluxed in glacial acetic acid for 10 min and allowed to stand overnight. The crude product was obtained upon cooling. 3). The oil 23 was dissolved in methanol, a drop of concentrated sulfuric acid added, and the solution refluxed for 10 min. The crude product 16 again separated upon cooling. These were the only known preparations for 16.

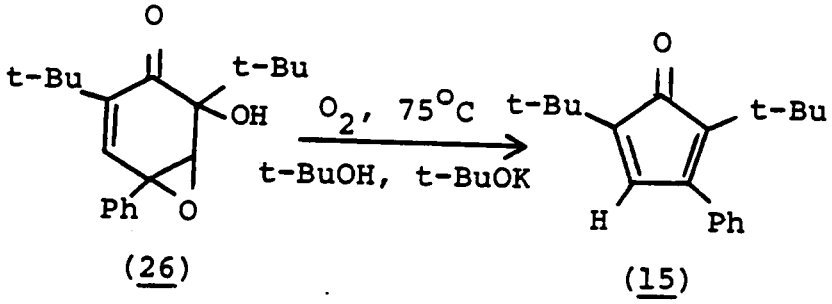




d. Preparation of 2,5-Di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one(15)

The title compound was first synthesized by A. Nishinaga, et al.[15] They prepared 2,5-di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (15) by reacting 4-phenyl-2,6-di(t-butyl)phenol (25) with potassium t-butoxide in the presence of oxygen, using t-butyl alcohol as a solvent. The reaction time was 6 h at a temperature of 75°C. The crude products 15 and (epoxy-o-quinol) (26) were purified first by chromatography and later by recrystallization. The co-product 26 could also be reacted under similar conditions for 3 h to give 15. These were the only known preparations for 15.

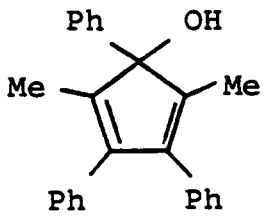




2. Previous Synthetic Procedures For The Preparation of 2,5-Dialkyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ols

Preparation of 2,5-Dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8)

This alcohol was the only alcohol of the studied series that had been previously prepared. However, there was no report of its synthesis in the literature because Allen and Van Allen[8] misidentified the product of their reaction as 2,5-dimethyl-3,3,4-triphenyl-1,4-cyclopentadien-1-ol (12) rather than 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8).



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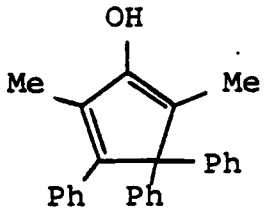
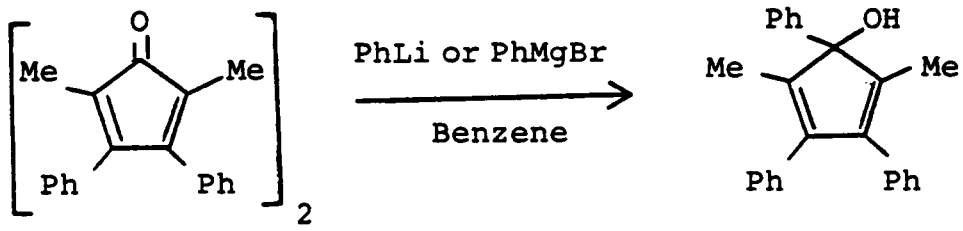


(12)

The stable enol 12 was postulated on the basis of analysis of the products obtained from the oxidation of 8. The structure of Allen and Van Allen's product has been correctly assigned in this work as 8.

The only synthesis of this molecule reported is that of by Allen and Van Allen.[8] They reacted the 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13) with either phenyllithium or phenylmagnesium bromide in refluxing benzene for 6-18 hours. The crude product 8 was purified first by vacuum distillation and later by recrystallization from either isopropanol or heptane.



(14) (8)

III. Experimental

A. General

All ^{1}H NMR spectra were obtained on a Varian EM-390, ^{13}C NMR's were performed on an IBM NR-80; 80 mHZ NMR, and 200 MHZ ^{1}H NMR's were performed on an Oxford IBM 200 MHZ NMR. Melting points were obtained using a Thomas-Hoover melting point apparatus and are uncorrected, while IR spectra were obtained using a Perkin Elmer 710-B Dual Beam Infrared Spectrophotometer. All lc analyses were performed using a Molecular Separations Incorporated Model B-500 Liquid Chromatograph with an Instrumentation Specialities Company U-V detector. The column used was a Micro Pak NH_2-10 column (30 cm X 4 mm).

B. Synthetic

1. Synthetic Methods For the Preparation of Hindered Cyclopentadien-1-ones.

Although the primary goal of this study was the synthesis and rearrangement of the previously described alcohols, another goal was the synthesis of 2,5-dialkyl-3,4-diphenyl-2,4-cyclopentadien-1-ones in which the alkyl groups were isopropyl, cyclohexyl, and t-butyl. The reasons for preparing these compounds were two-fold. First, it was felt that although earlier experiments[12] had not caused the formation of these compounds even under forced conditions, the

current availability of stronger bases would make the reactions possible. Second, these hindered compounds were to be used as the object of studies similar to those described in this thesis.

The procedures used in the attempts at the synthesis of these compounds are described in this section.

a. Preparation of Hindered Ketones

Two ketones that were needed in the synthesis of the hindered cyclopentadienones were not available commercially but were reported in the literature. These ketones were prepared using the literature procedures.

i. Preparation of 1,3-Dicyclohexyl-2-propanone (37)

The title compound was prepared using essentially the procedure of Grier, et al.[16] Into a 100 mL 3-necked round-bottomed flask equipped with an overhead stirrer, a water-cooled reflux condenser, a nitrogen inlet, and a heating mantle were placed 10 g (0.0705 mol) of cyclohexylacetic acid and 2.1 g (0.0385 mol) of hydrogen reduced iron (Aldrich Chemical Co.). The mixture was stirred and heated to 230°C with hydrogen evolution beginning at about 160°C. The temperature was maintained at 230°C for 1 h, raised gradually to 290°C, and maintained there for 3 hours. After that time the reaction mixture was poured into a mortar and allowed to cool and harden before being ground into a fine

powder. The powder was extracted repeatedly with ether so that all of the product would be separated away from the iron filings. The ether extract was washed with 200 mL of a 5% solution of sodium bicarbonate in water, dried over anhydrous magnesium sulfate, and the ether evaporated to a reddish oil. The oil was purified using column chromatography (20 cm, Neutral alumina). A light-colored band, quickly eluted, was collected and evaporated to afford an oil 1,3-dicyclohexyl-2-propanone (37), 3.4 g (0.016 mol, 44%).

ii. Preparation of 2,2,6,6-Tetramethyl-4-heptanone (38)

The synthesis of the title compound was accomplished using essentially the procedure described in Organic Synthesis.[17] Into a 500 mL 3-necked round-bottomed flask equipped with a stirring bar, an addition funnel, a water-cooled reflux condenser, a ground glass stopper, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 3 g (0.21 mol) of magnesium, 5 g (0.047 mol) of neopentyl chloride, and 60 mL of freshly dried and distilled diethyl ether. The mixture was stirred at reflux under nitrogen and to it was added 10.6 g (0.056 mol) of ethylene dibromide in 20 mL of the anhydrous diethyl ether over 12 hours. After 1 h the addition was stopped and a small amount of ethylene dibromide was added directly to the reaction mixture to aid in starting the reaction. Once the reaction had started (as evi-

denced by the development of a grayish color), addition of the remainder of the solution continued. After the addition was complete, the reaction mixture was stirred at reflux for 2 h, cooled to 0 - -5°C, and to it was added 5.1 g (0.038 mol) of t-butylacetyl chloride in 15 mL of the anhydrous diethyl ether over 90 min. The reaction mixture was stirred for an additional 90 min at 0 to -5°C, after which time it was poured over a mixture of 60 g of ice in 12 mL of concentrated hydrochloric acid. The mixture was placed in a separatory funnel, the aqueous layer separated, and the organic layer extracted separately with 25 mL portions of water, 5% sodium bicarbonate in water, and a saturated aqueous sodium chloride solution. The aqueous layers were combined, acidified, and extracted with ether to obtain any t-butylacetic acid that was formed as a by-product of the reaction and work-up. In general, very little t-butylacetic acid was obtained in this manner. The organic phase was dried over anhydrous magnesium sulfate and the dried solution evaporated to an oil using a rotovaporator. Thus 4.1 g (0.026 mol, 67.8%) of crude 2,2,6,6-tetramethyl-4-heptanone (38) was obtained. The product was further purified by vacuum distillation, 38-40°C at 0.1 mm, to give 3.14 g (0.019 mol, 50%) of pure 38.

iii. Preparation of t-Butylacetyl Chloride From t-Butylacetic Acid.

The t-butylacetic acid which was collected from the previous reaction was converted to t-butylacetyl chloride using an Organic Synthesis preparation.[18] Into a 50 mL 1-neck round-bottomed flask equipped with a stirring bar and a water-cooled reflux condenser were placed 9.5 g (0.082 mol) of t-butylacetic acid and 8 mL (13 g, 0.11 mol) of thionyl chloride. The reaction was stirred for 3 h at room temperature and then heated at 80°C for an additional hour. After this time the reaction was distilled under nitrogen, to give 6.5g (0.048 mol, 59.2%) of pure t-butylacetyl chloride, bp 126-132°C. This compound was then used as previously described.

b. Base Reactions Using 4-Heptanone As Model Ketone.

In order to establish the effectiveness of selected bases in the condensation reaction, 4-heptanone was used as a model ketone. This ketone, when reacted with benzil in the presence of a mild base, formed 2,5-diethyl-3,4-diphenyl-2-cyclopenten-4-ol-1-one (22) in high yield. Since this reaction was not hampered by steric hindrance, it was felt that if the bases used did not affect condensation of the model compound, they could be considered as having little chance of affecting condensation in the hindered cases.

i. Reactions Using Potassium Hydroxide As Base

The procedure was essentially that listed in Fieser.[19] Into a large heavy-walled test tube were placed 10 mL of triethylene glycol, 2.1 g (0.01 mol) of benzil, and 2.8 mL (2.29 g, 0.016 mol) of 4-heptanone. This mixture was heated gently to dissolve the reactants and then to raise the temperature to 100°C. To this solution one gram of potassium hydroxide in 8 mL of triethylene glycol (preheated to 100°C) was added and the mixture was stirred once. At that time the temperature was reduced to 80°C and the solution poured into 60 mL of water. The mixture was stirred and left to precipitate. The yellow crystals which had formed were filtered, washed with ethanol, and left to dry. The crude yield for this reaction was 66%, but only 13% of purified product was obtained. It was also found that if the above procedure was followed except that the potassium hydroxide was added at the start of the reaction and heated along with the other reactants, the alcohol 2,5-diethyl-3,4-diphenyl-2-cyclopenten-4-ol-1-one (22) was obtained in 19% yield.

ii. Reactions Using Triton-B As Base With Ethyl Alcohol As Solvent

Into a 125 mL Erylenmeyer flask were placed 2.1 g (0.01 mol) of benzil, 2.8 mL (2.3 g, 0.016 mol) of 4-heptanone, 30 mL of absolute ethyl alcohol, and 1.5 mL of N-benzyltrimet-

hylammonium hydroxide (Triton-B). The mixture was stirred to effect solution and then allowed to stand for an additional 72 hours. At that time the reaction mixture was poured into 75 mL of water, the resulting mixture allowed to stand for several hours, and the solid which had formed was filtered and dried. In this manner 2.1 g (0.0069 mol, 69%) of crude 22 were obtained. The purity of the crude material was similar to that reported by Allen and Van Allen.[14]

The same procedure was used again with the exception that the solution was refluxed after the addition of the base. The product obtained from this reaction was an oil which was not the desired compound.

iii. Reactions Using Lithium Diisopropyl Amide As Base

The procedure followed for lithium diisopropyl amide (LDA) preparation was essentially that of Dupont.[20] Into a 250 mL 3-necked round-bottomed flask equipped with an addition funnel, a stirring bar, a water-cooled reflux condenser, and a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), was placed 40 mL of freshly dried and distilled tetrahydrofuran (THF). The THF was cooled to -78^{o}C by means of a dry ice-isopropanol bath and to it was added 5.1 g of diisopropylamine (0.051 mol). Then 16 mL (0.04 mol) of a 2.5 molar solution of methyllithium in hexane were added slowly to the reaction mixture and the resulting solution stirred for 30 min. After that time 1.15

g (0.01 mol) of 4-heptanone in 10 mL of THF were added over 1 h and the solution stirred for an additional hour. The reaction mixture was allowed to slowly warm to room temperature and was then refluxed using a heating mantle. After the solution had refluxed for 15 min., 1.05 g (0.005 mol) of benzil in 15 mL of THF were added over 50 min. The reaction was further refluxed for 4 h after which time it was quenched with ammonium chloride, washed with water, and the organic phase dried over anhydrous magnesium sulfate. The dried solution was evaporated to an oil using a rotovaporator, the oil dissolved in 95% ethyl alcohol, and the ethanol solution poured into water. Upon addition to the water, crystals formed, were filtered, and dried. In this manner 0.7 g (0.002 mol, 46%) of 2,5-diethyl-3,4-diphenyl-2-cyclopenten-4-ol-1-one (22) was obtained.

The following bases were tried but were unsuccessful in achieving the desired condensation.

iv. Reaction Using Triton-B As Base With Triethylene Glycol As Solvent

The procedure used was essentially that of listed in Fieser and Fieser.[18] Into a large heavy-walled test tube were placed 2.1 g (0.01 mol) of benzil, 1.15 g (0.01 mol) of 4-heptanone, and 10 mL of triethylene glycol (TEG). This mixture was heated gently at first to cause solution to occur and then to raise the temperature to 100°C. At that

temperature 1 mL of Triton-B was added and the solution stirred once. The reaction mixture was allowed to cool to 80°C, 5 mL of methanol was added, and the solution poured into 75 mL of water. Upon filtration and analysis of the crystals which had formed, it was found that only the starting material was recovered.

v. Reactions using Sodium Amide as base.

The procedure used was essentially that of Kenyon, et al.[21] Into a 250 mL 3-necked round-bottomed flask equipped with a stirring bar, an addition funnel, and an air-cooled condenser column equipped with a dry ice-isopropanol trap was added 75 mL of liquid ammonia. To this was added 1.35 g (0.035 mol) of sodium amide and the resulting mixture stirred for 90 min. Then 1.44 g (0.013 mol) of 4-heptanone in 20 mL of freshly dried and distilled diethyl ether was added over 20 min. After this mixture was stirred for 40 min, 1.05 g (0.005 mol) of benzil in 20 mL of the anhydrous diethyl ether was added over 15 min. This solution was stirred for 6 h, and then was quenched by adding 1.8 g (0.034 mol) of ammonium chloride along with 25 mL each of water and diethyl ether. The ammonia was allowed to evaporate, the aqueous layer separated, the organic layers dried over anhydrous magnesium sulfate, and the dried solution evaporated to an oil using a rotovaporator. The analysis of the oil showed no evidence of any condensation.

This reaction was also run using diethyl ether and benzene as solvents. However, no better results were obtained.

c. Attempts To Synthesize 2,5-Diisopropyl-3,4-diphenyl-2-cyclopenten-4-ol-1-one

i. Quenching Experiments

In order to etablish that the anion needed for the reaction was being formed, 2,6-dimethyl-4-heptanone was reacted with LDA and the anion quenched separately with D_2O, benzylchloride, and benzaldehyde. Only the reaction which used benzaldehyde to quench the anion gave acceptable proof of anion existence.

aa. Reactions Quenched With D_2O and Benzylchloride

The procedure to make the lithium diisopropyl amide (LDA) was essentially that of Dupont[20] for the quenching experiments. Into a 200 mL 3-necked round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, an addition funnel, a nitrogen inlet, a glass stopper (all of which had been oven-dried and cooled under nitrogen), and a dry ice-isopropanol bath were placed 3.5 mL (2.53 g, 0.025 mol) of diisopropylamine and 75 mL of freshly dried and distilled diethyl ether. To this cooled solution was added slowly 8 mL (0.02 mol) of a 1.8 molar solution of methyllithium in diethyl ether and the resulting solution stirred for 20 min. After this time 2.8 mL (2.4 g, 0.017

mol) of 2,6-dimethyl-4-heptanone in 25 mL of the anhydrous diethyl ether was added dropwise over 1 hour. The solution was stirred for an additional hour before samples were taken and quenched using D_2O and benzyl chloride. After sampling, the solution temperature was allowed to rise to room temperature and then stirred for 30 min. At that time samples of the reaction were quenched as previously described. Similar experiments were performed after the reaction mixture had been refluxed for 30 min. To determine if the anion had been quenched, NMR analysis of the crude samples was performed. It appeared that some quenching had taken place, but the results were not conclusive.

bb. Reactions Quenched With Benzaldehyde

In order to determine conclusively that the anion was formed and that it would react with ketones similar in structure to benzil, the anion was quenched with benzaldehyde using the following procedure. Into a 200 mL 3-necked round-bottomed flask equipped with a stirring bar, an addition funnel, a water-cooled reflux condenser, a nitrogen inlet, a glass stopper (all of which had been oven-dried and cooled under nitrogen), and a dry ice-isopropanol bath were placed 5.2 mL (3.75 g, 0.037 mol) of diisopropylamine, and 20 mL of freshly dried and distilled tetrahydrofuran (THF). To this stirred solution was added slowly 12 mL (0.03 mol) of a 2.5 molar solution of methyllithium in diethyl ether.

After 15 min, 1.7 mL (1.44 g, 0.01 mol) of 2,6-dimethyl-4-heptanone in 30 mL of the anhydrous THF was added over 1 h and the solution stirred for another hour. At that time the solution was allowed to warm to room temperature and then refluxed for 90 min. To the resulting clear yellow solution was added 1.1 mL (1 g, 0.011 mol) of benzaldehyde in 20 mL of the anhydrous THF over 30 min. During the addition the solution color changed from the yellow to light orange and back to yellow. The solution was refluxed for 90 min after the addition was complete. The flask was then cooled, 1.5 g (0.028 mol) of ammonium chloride added, and the contents of the flask poured into a separatory funnel and washed three times with 50 mL portions of water. The organic layer was dried over anhydrous magnesium sulfate and the dried solution evaporated to an oil using a rotovaporator. The oil was analyzed by both IR and NMR. The IR (3660 cm^{-1}, OH) spectrum clearly showed that the anion had reacted with the benzaldehyde to form an alcohol. However, there appeared to be some unreacted benzaldehyde present. The NMR spectrum also confirmed that the condensation had occurred. Integration showed that the ratio of benzaldehyde to alcohol was 13/87.

ii. Reactions of 2,6-Dimethyl-4-heptanone and Benzil Using Selected Bases

Since the existence and reactivity of the anion had been proven, condensation of 2,6-dimethyl-4-heptanone with benzil using a variety of bases was attempted. The following procedures are examples of the reactions tried.

aa. Reactions Using Potassium Hydroxide As Base

The procedure used was essentially that of Allen and Van Allen[12]. Into a 100 mL round-bottomed flask equipped with a stirring bar and drying tube were placed 4.2 g (0.02 mol) of benzil, 6.7 mL (5.7 g, 0.04 mol) of 2,6-dimethyl-4-heptanone, and 50 mL of anhydrous ethyl alcohol containing 0.2 g of potassium hydroxide. The mixture was stirred to obtain solution and allowed to stand for 96 h before being poured into 250 mL of water. The precipitate which formed was filtered, analyzed, and found to be benzil. There was no evidence of any reaction having taken place.

The reaction was also performed at a higher temperature. The procedure used was essentially that listed in Organic Synthesis[22] Into a 500 mL round-bottomed flask equipped with a stirring bar and a water-cooled reflux condenser was placed 21 g (0.1 mol) of benzil, 17 mL (14.4 g, 0.1 mol) of 2,6-dimethyl-4-heptanone, and 150 mL of absolute ethyl alcohol. The mixture was stirred to solution, brought to reflux, and to it added in two portions 3 g of potassium

hydroxide in 18 mL of absolute ethyl alcohol. Upon addition of the base, the solution frothed, became deep purple, and was refluxed for 15 min before being cooled to 0°C by means of a ice-water bath. The dark precipitate which had formed was filtered and washed with 95% ethyl alcohol. The tan crystals which remained were analyzed by IR and found to be a mixture of benzil and benzilic acid. Otherwise no reaction was found to have occurred.

A similar reaction was tried using methyl alcohol as solvent. Again no condensation took place.

bb. Reactions Using Triton-B As Base

The procedure used was essentially that listed in Fieser.[20] Into a 50 mL heavy-walled test tube were placed 2.1 g (0.01 mol) of benzil, 1.42 g (0.01 mol) of 2,6-dimethyl-4-heptanone, and 10 mL of triethylene glycol. The mixture was heated first gently to cause solution and then to raise the temperature of the solution to 100°C. At this point 1 mL of a 40% solution of Triton-B in methanol was added and the solution stirred once. The solution was allowed to cool to 80°C, cooled further with tap water, 10 mL of methanol added, and the solution poured into water. The precipitate which had formed was filtered and found to be benzil. No reaction had taken place.

The reaction was also performed using Triton-B as base but using absolute ethyl alcohol as solvent. Into a 50 mL round-bottomed flask equipped with a stirring bar and a water-cooled reflux condenser were placed 2.1 g (.001 mol) of benzil, 1.7 mL (1.44 g, .001 mol) of 2,6-dimethyl-4-heptanone, and 22 mL of absolute ethyl alcohol. This solution was stirred and heated almost to reflux and 1.2 mL of Triton-B (40% in methanol) was added through the reflux condenser. The solution turned slowly from yellow to deep purple and was refluxed for 20 min. The solution was cooled in ice and the crystals which had formed were filtered. Once again there was no condensation.

When methanol was used as solvent for the above reaction, the same results were obtained.

cc. Reactions Using Lithium Diisopropyl Amide As Base

The procedure to make the lithium diisopropyl amide was essentially that of Dupont[20] as was presented earlier. To the LDA solution was added 1.42 g (0.01 mol) of 2,6-dimethyl-4-heptanone in 30 mL of the anhydrous THF over 1 h and the entire mixture stirred for another hour. The solution was allowed to warm to room temperature and later refluxed for 30 min. To the clear yellow solution was added 2.1 g (0.01 mol) of benzil in 8 mL of the anhydrous THF over 45 min. The solution became gradually darker as the benzil was added and was refluxed for 4 h after the addition was

complete. The reaction mixture was quenched by adding 2 g of ammonium chloride to the mixture. The organic phase was then extracted with water (3 x 500 mL), dried over anhydrous calcium sulfate, and the dried solution evaporated to an oil using a rotovaporator. Analysis of the oil showed that a mixture of the starting materials had been recovered.

dd. Reactions Using Sodium Amide As Base

The procedure used to prepare the basic solution was essentially that of Kenyon, et al.[21] Into a 200 mL 3-necked round-bottomed flask equipped with a stirring bar, an additional funnel, a water-cooled reflux condenser, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 1.44 g (0.01 mol) of 2,6-dimethyl-4-heptanone and 45 mL of freshly dried and distilled diethyl ether. To this stirred solution was added 0.9 g (0.023 mol) of sodium amide powder, and the mixture was stirred at reflux for 3 hours. After this time the reaction mixture was cooled to 0^{o}C by means of an ice-water bath and to it was added 2.1 g (0.01 mol) of benzil in 25 mL of the anhydrous diethyl ether. The solution was then refluxed for 1 h before being quenched with 2 g of ammonium chloride. The quenched solution was then washed with water, dried over anhydrous magnesium sulfate, and the dried solution evaporated to an oil using a rotovaporator. Analysis of the oil by IR indicated that no reaction had occurred.

2. Synthetic Methods For The Preparation of Precursor Ketones

a. Preparation of 2,5-Dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13)

The title compound was prepared using essentially the procedure of Gray[9], starting from 2,5-dimethyl-3,4-diphenyl-2-cyclopenten-4-ol-1-one (17). The alcohol 17 was prepared using the procedures of Japp and Meldrum.[10] The methods of preparation for these compounds, with the method of choice presented first, are described as follows.

Into a 250 mL round-bottomed flask equipped with a magnetic stirring bar and drying tube were introduced 10 g (0.048 mol) of benzil (18), 7.9 g (0.096 mol) of 3-pentanone (19), and 100 mL of absolute ethyl alcohol containing 0.4 g of dissolved potassium hydroxide (0.5% KOH/ethanol). The reactants were stirred until dissolved and allowed to react for 96 hours. After this time, the tea-colored solution was poured into 300 mL. of water. The crystals that formed were filtered and dried to give 12.5 g (0.045 mol, 94%) of crude 17, mp 149-150°C, [Lit.[10] 150°C]. The alcohol could be purified by recrystallization from 95% ethyl alcohol or reacted in its crude form to give 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13). The above reaction was also performed on a scale of twice the given amount with no decrease in yield.

The alcohol 17 was also produced in the following manner. Into a 50 mL round-bottomed flask equipped with magnetic stirring bar and water-cooled reflux condenser were placed 4 g (0.019 mol) of benzil (18), 3 g (0.035 mol) of 3-pentanone (19), and 3 mL of 33% aqueous potassium hydroxide. The reaction mixture was heated at 65°C for 1.5 h, during which time the benzil slowly dissolved and new crystals of the product began to form. The reaction mixture was left at room temperature for the remainder of the 24 h and then poured into 200 mL of hot water. Upon mixing with the water, the reaction mixture became an oil which, when cooled, became a hard crystalline mass. The mass of crystals were pulverized and washed first with hot water and later with diethyl ether, with most of the crystals dissolving in the diethyl ether. The ether layer was evaporated to give 3.1 g (0.011 mol, 58%) of a mixture of yellow and white crystals, mp 110-114. The crystals which did not dissolve in the diethyl ether were recrystallized from 95% ethyl alcohol to give 0.5 g (0.0018 mol, 9.4%) of white crystals, mp 130-133°C. The combined crude yield of both isomers of 17 was 67.4%.

The dimer 13 was then prepared from crude 17 in the following manner. Into a 50 mL round-bottomed flask equipped with a magnetic stirring bar were placed 1.8 g (0.0065 mol) of 17 and 5 mL of acetic ahydride. To this stirred suspension was added 2 drops of concentrated sulfuric acid.

The crystals of 17 dissolved, the solution became faint green, and crystals of 13 began to form. The reaction mixture was stirred for an hour and then poured into 50 mL of water. The crystals were filtered, dried, and recrystallized from ethyl acetate to give 1g (0.0019 mol, 62%) of 13, mp 181-183°C dec, (Lit.[11] 181-182°C dec).

b. Preparation of 2,5-Diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14).

The title compound was prepared using essentially the procedure of Allen and Van Allen [12] from 2,5 diethyl-3,4-diphenyl-2-cyclopenten-4-ol-1-one (21). The alcohol 21 was produced using the following procedure. Into a 500 mL round-bottomed flask equipped with a magnetic stirring bar and drying tube were placed 21 g (0.1 mol) of benzil (18), 23 g (0.2 mol) of 4-heptanone (22), and 250 mL of absolute ethyl alcohol containing 1 g of dissolved potassium hydroxide (0.5% KOH/ethanol). The solution was stirred until all of the reactants had dissolved. The reaction mixture was allowed to react for 96 h, after which time it was poured into 400 mL of water. Upon mixing the reaction solution with water, crystals of the product formed and were filtered, dried and normally reacted in the crude form to give 2,5-diethyl- 3,4-diphenyl-2,4-cyclopentadien-1-one (14). The yield of crude product was 28.8 g (0.094 mol, 94%), mp 108-110°C. The crude product could be recrystallized using

95% of ethyl alcohol to give pure crystals, mp 110.5-112°C (Lit.[12] 113-114°C).

Once 21 was obtained, it was dehydrated using the following procedure. Into a 50 mL round-bottomed flask equipped with a magnetic stirring bar were placed 5 g (0.016 mol) of 21 and 20 mL of acetic anhydride. To this stirred suspension was added several drops of concentrated sulfuric acid. The suspension quickly became a bright red solution and was stirred for an additional hour before being poured into 75 mL of water. Upon mixing with the water, the initially formed oil soon formed bright red crystals. The crystals were filtered, dried, and recrystalized from 95% ethyl alcohol. The purified crystals were placed under vacuum to remove residual solvent. In this manner 3.2g (0.011 mol, 68.8%) of pure 14 were obtained, mp 100.5-101.5°C (Lit.[14] 103°C). The dienone 14 was found to decompose upon standing and was produced and purified as needed from 21.

c. Preparation of 15,16-Diphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-one (16).

The title compound was prepared using essentially the procedure of Allen and Van Allen [14] by dehydration of 15,16-diphenylbicyclo[12.2.1]heptadeca-14-en-16-ol-17-one (23). The following procedure was used to prepare 23. Into a 50 mL round-bottomed flask equipped with a stirring bar and an air-cooled reflux condenser were added 1 g

(0.005 mol) of cyclopentadecanone (24), 1.3g (0.0062 mol) of benzil (18), and 2 g (0.05 mol) of potassium hydroxide which had been dissolved in 13 mL of methanol. The reaction mixture was stirred vigorously for 24 h during which time crystals of 23 formed. The reaction mixture was then poured into 50 mL of water and the precipitate filtered to give 1.8g (0.0043 mol, 87%) of crude 23. The alcohol 23 was reacted in its crude form because attempts at purification were unsuccessful. The reaction was also attempted using equal molar amounts of both 18 and 23[16], but otherwise using similar conditions. The products from these reactions were oils which were contaminated with unreacted 18.

Once 23 was obtained in its crude form, the preparation of 15,16-diphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-one (16) was accomplished in the following manner. Into a 50 mL round-bottomed flask equipped with a stirring bar were placed 1.85 g (0.0044 mol) of 23 and 8 mL of acetic anhydride. To this stirred suspension was added 2 drops of concentrated sulfuric acid. Upon addition of the acid, the suspension became a bright red solution. The solution was stirred and heated at 70°C for 5 min, allowed to cool to room temperature, and then cooled to 0°C by means of an ice-water bath. When the solution was cooled, orange crystals of 16 soon formed and were filtered. The crude product was purified by recrystallization from methanol to give 1.2 g (0.003 mol, 67%) of pure 16, mp 113-114°C (Lit.[14] 111°C).

d. Preparation of 2,5 Di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (15).

The title compound was prepared by a three step synthesis. The starting material for the synthesis, 2,6-di(t-butyl) p-benzoquinone (27), was obtained from Aldrich Chemical Co. The following procedures were used to convert 27 to 2,5-di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (15).

i. Preparation of 2,6-Di(t-butyl)-4-phenyl-2,5-cyclohexadien-4-ol-1-one (28) from 2,6-Di(t-butyl) p-benzoquinone (27)

The title compound was prepared from 2,6-di(t-butyl) p-benzoquinone (27) using essentially the procedure of Rieker and Zienek.[23] Into a 100 mL 3-necked microware round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, a 50 mL addition funnel, a nitrogen inlet (the whole of which had been oven-dried and cooled under nitrogen) and a heating mantle were placed 0.3 g (0.012 moles) of magnesium, 5 mL of freshly dried and distilled diethyl ether, and a few drops of both ethylene dibromide and bromobenzene. After the reaction had started a solution of 1.4 g (0.009 mol) of bromobenzene and 10 mL of dry diethyl ether was added slowly. When the addition was complete, the entire solution was refluxed for 1.5 hours.

The Grignard solution was then cooled, decanted into an addition funnel, and added slowly to 2 g (0.0091 mol) of 27 which had been dissolved in dry diethyl ether. The resulting reaction mixture was refluxed for an additional 2 h and quenched with 10 mL of 10% by weight solution of ammonium chloride in water. The ether layer was separated from the aqueous layer using a separatory funnel and the aqueous layer extracted 3 times with 30 mL portions of diethyl ether. The combined ether fractions were dried over anhydrous sodium sulfate, the dried solution evaporated to an oil using a rotovaporator, and the oil purified by recrystallization from diethyl ether and petroleum ether (50/50). The oil thus purified yielded 1.6 g (0.005 mol, 59.6%) of 2,6-di(t-butyl)-4-phenyl-2,5-cyclohexadien-4-ol-1-one (28), mp 137.5-139.5°C (Lit.[18] 136-138°C).

ii. Preparation of 2,6-Di(t-butyl)-4-phenyl phenol (29) from 2,6-Di(t-butyl)-4-phenyl-2,5-cyclohexadien-4-ol-1-one (28).

The title compound was prepared from 2,6-di(t-butyl)-4-phenyl-2,5-cyclohexadien-4-ol-1-one (28) using essentially the procedure of Rieker and Scheffler.[24] Zinc dust was activated using the following procedure of Yamamura.[25] Zinc dust was washed with 2% hydrochloric acid for 3 min. After this time the acid was removed and the zinc washed repeatedly and separately with water, absolute ethyl alcohol, acetone, and

anhydrous diethyl ether. The zinc dust was then heated at 90°C under vacuum using a rotovaporator, without spinning, for 10 min and allowed to sit overnight under nitrogen (at least 10-12 h) before use. The zinc, thus activated, was used in the following procedure.

Into a 100 mL 3-necked microware round-bottomed flask equipped with an addition funnel, a stirring bar, a water-cooled reflux condenser (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 2 g (0.007 mol) of 28, 2 g (0.03 mol) of activated zinc, and 20 mL of methanol. To this stirred mixture was added, by means of an addition funnel, 20 mL of concentrated hydrochloric acid. Hydrogen evolution began immediately. The reaction mixture was heated at reflux for 24 h, after which time white crystals had formed in the reaction mixture and the zinc was mostly reacted. The product was purified by performing a hot filtration of the reaction mixture through fluted filter paper using methanol as solvent. The reaction flask was rinsed repeatedly with hot methanol to dissolve the product. In this manner the product was separated from the unreacted zinc. The product which slowly crystallized from the methanol mixture was filtered to give 1.6 g (0.0057 mol, 81%) of pure 2,6-di(t-butyl)-4-phenyl phenol (29), mp 102-103°C (Lit.[19] 100-101°C).

iii. Preparation of 2,5-Di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (15) from 2,6-Di(t-butyl)-4-phenyl phenol (29)

The title compound was prepared from 2,6-di(t-butyl)-4-phenyl phenol (29) using essentially the procedure of Nishinaga, et al.[15] Into a 50 mL 3-necked microware round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, and an oxygen inlet (all of which had been oven-dried and cooled under nitrogen) were placed 0.56 g (0.002 mol) of 29, 0.56 g (0.005 mol) of potassium tertiary-butoxide, and 15 mL of t-butyl alcohol. The reaction mixture was stirred at 75°C and oxygen bubbled through it for 6 hours. At this time the reaction mixture had turned orange and was poured into 50 mL of a 10% by weight solution of ammonium chloride in water. The solution was transferred to a separatory funnel and extracted 3 times with 30 mL portions of diethyl ether. The ether layers were combined, washed with water, dried over anhydrous sodium sulfate, and the dried solution evaporated to an oil by means of a rotovaporator. The oil was purified via a 20 cm silica gel column using petroleum ether as the solvent. Sufficient petroleum ether was used in order to completely elute the orange band from the column. The orange band was collected and evaporated to an oil which slowly crystalized. The crystals that formed were filtered and purified by recrystallization from methanol. In this manner 0.123 g (0.00046

mol, 22.9%) of 2,5-di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (15) was obtained, mp 100-101°C (Lit.[15] 97-98°C). The column was further eluted with sufficient petroleum ether and methylene chloride (9:1) to completely elute the yellow band from the column: epoxy-o-quinols (26). Attempts at purification of 26 and its subsequent use as a reactant in the preparation of 15 were unsuccessful. It was found that 15 could be purified from the crude reaction mixture by repeated recrystallization rather than using a silica gel column and then recrystallization. However, there was no evidence to suggest that this method of purification was any better than the previous method.

e. Preparation of 2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-one (2)

The title compound was prepared using two procedures, both of which will be presented here. The first procedure was essentially that described in Fieser.[19] Into a 50 ml heavy-walled test tube were placed 2.1 g (0.01 mol) of benzil (18), 2.1 g (0.01 mol) of dibenzyl ketone (30), and 10 ml of triethylene glycol (TEG). The mixture was heated gently to dissolve 18 and then to raise the temperature of the solution to 100°C. At this point 1 mL of a 40% solution of n-benzyltrimethylammonium hydroxide in methanol (Triton-B) was added and the solution stirred once to mix. The solution became dark (purple-black) and crystals formed.

This mixture was allowed to cool to 80°C and then further cooled with tap water. After cooling, 10 mL of methanol was added, the reaction mixture filtered, and the product washed with methanol until the wash solution became purple-pink and not brown. In this manner 3.5 g (0.0091 mol, 91%) of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (2) were obtained. The melting point of the product was consistent with literature values without further purification, mp 218-220°C (Lit.[19] 219°C).

The second procedure used was essentially that found in Organic Synthesis.[22] Into a 250 ml round-bottomed flask equipped with a stirring bar and a water-cooled reflux condenser were placed 12.6 g (0.0595 mol) of benzil (18), 12.6 g (0.0595 mol) of dibenzyl ketone (30), and 65 ml of 95% ethyl alcohol. The solution was brought to reflux and to it was added in two portions 1.3 g (0.0325 mol) of potassium hydroxide in 6.5 mL of 95% ethyl alcohol. The reaction mixture became dark purple and was heated for an additional 30 min. After this time, the reaction mixture was cooled to 0°C and the product filtered, washed 4 times with 5 mL portions of 95% ethyl alcohol, and air dried. In this manner 18.5 g (0.048 mol, 80.9%) of 2 were obtained. The product was used without further purification.

3. Synthetic Methods For The Preparation of 2,5-Dialkyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ols

The alcohols that were needed for the rearrangements and kinetic studies were prepared from the precursor ketones. All of the alcohols except for those prepared from 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13) and parent alcohol were unknown in the literature. With the exception of 2,5-di(t-butyl)-1,3-diphenyl-2,4-cyclopentadien-1-one (15) all ketones were reacted with both phenyllithium and phenylmagnesium bromide as reagents to prepare the alcohols. This was done to establish if one of the reagents would be better in the reactions with these ketones. The procedures used to form the alcohols from the ketones are listed here.

a. Preparation of 2,5-Dimethyl-1-anisyl-3,4-diphenyl-2,4-cyclopentadien-1-ol (31) From 2,5-Dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13).

The synthesis of the title compound was accomplished using essentially the procedure of Allen and Van Allen [8] from 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13). Into a 250 ml 3-necked round-bottomed flask equipped with a magnetic stirring bar, a water-cooled reflux condenser, an addition funnel, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 1.1 g (0.044 mol) of magnesium,

20 ml of freshly dried and distilled diethyl ether, and a few drops of both ethylene dibromide and p-bromoanisole. After the reaction had started, 7.5 g (0.04 mol) of p-bromoanisole in 15 mL of the anhydrous diethyl ether was added dropwise to the stirred solution. The rate of addition was regulated to control the reaction rate. After the addition was complete, the reaction continued for another 35-40 min. At this time 25 mL of dry benzene was added to the reaction mixture, and to the resulting solution was added 2.6 g (0.005 mol) of 13 in 50 mL of hot dry benzene over 30 min. The reaction mixture was stirred and heated to remove the diethyl ether and then at reflux via a steam bath for 21 h, cooled in ice, and quenched with 17 mL of acetic acid in 70 mL of water. The solution was transferred to a separatory funnel and the aqueous layer separated and extracted with 50 mL of benzene. The organic layers were combined, washed with water, dried over anhydrous magnesium sulfate, and the dried solution evaporated via a rotovaporator to a yellow residue. The residue, when cooled and filtered gave impure 2,5-dimethyl-1-anisyl-3,4-diphenyl-2,4-cyclopentadiene-1-ol (31). The crude product was purified by recrystallization from benzene to give 0.3 g (0.009 mol, 9%) of pure 31, mp 191.5-193.5°C (Lit.[16] 193-194°C).

b. Preparation of 2,5-Dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8) From 2,5-Dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13).

The title compound was synthesized using essentially the procedure of Allen and Van Allen[8] from the dimer using both Grignard and phenyllithium.

i. Preparation of 2,5-Dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8) From 2,5-Dimethyl-2,4-cyclopentadien-1-one dimer (14) Using Grignard Reagent.

Into a 250 ml 3-necked round-bottomed flask equipped with a magnetic stirring bar, a water-cooled reflux condenser, an addition funnel, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen) and a heating mantle were placed 1.1 g (0.044 mol) of magnesium, 15 mL of freshly dried and distilled diethyl ether, and a few drops of both ethylene dibromide and bromobenzene. After the reaction had started, 6.3 g (0.04 mol) of bromobenzene in 35 mL of the anhydrous diethyl ether was added dropwise to the stirred solution over 30 min. When the initial reaction had subsided, the mixture was refluxed for an additional 30 min and 25 mL of dry benzene was added. Then 2.6 g (0.005 mol) of 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (13) in 50 mL of hot dry benzene was added to the stirred Grignard reagent over 10 min, the reaction mixture was first heated gently to remove the diethyl ether, and later heated

at reflux for 18 h using a steam bath. After that time the reaction mixture was cooled and quenched with a solution of 17 mL of acetic acid in 50 mL of water. The aqueous layer was separated using a separatory funnel and then extracted with 50 mL of benzene. The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, and the dried solution evaporated to an oil using a rotovaporator. The oil was found to crystallize upon sitting, but addition of isopropanol to the oil aided this occurrence. The product obtained in this manner was filtered, dried, and recrystallized from either isopropanol or methanol to give 1.1 g (0.003 mol, 33%) of pure 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8), mp 136-138°C (Lit.[8] 135-137°C). Both IR and NMR analysis were consistent with the proposed structure.

Anal: Calcd. for $C_{25}H_{22}O$: C, 88.72 ; H, 6.55

Found: C, 88.16 ; H, 6.68

MW (Mass spec) Calcd: 338

Found: 338

^1H NMR: ($CDCl_3$,TMS) 6.9-7.4(m,15), 2.1(s,1), 1.7(s,6)

IR: (CHl_3) 3660 cm^{-1},O-H

ii. Preparation of 2,5-Dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8) From 2,5-Dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (14) Using Phenyllithium

Into a 500 ml 3-necked round-bottomed flask equipped with a magnetic stirring bar, a water-cooled reflux condenser, a constant pressure addition funnel, a nitrogen inlet, a glass stopper (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 25 mL of freshly dried and distilled diethyl ether, 1.2 g (0.17 mol) of freshly cut lithium wire, and a few drops each of bromobenzene and dibromoethane. After the reaction had begun as evidenced by a grayish color, a solution of 13.8 g (0.088 mol) of bromobenzene in 15 mL of the anhydrous ether was slowly added. When the addition was complete and the reaction had subsided, the reaction mixture was refluxed for an additional 1.5 hours. At this time the reaction mixture was cooled to room temperature and to it added 5.8 g (0.011 mol) of 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one dimer (14) in 300 mL of hot benzene. After the addition was complete, the diethyl ether was allowed to evaporate. The remaining solution was refluxed for 19 h before being cooled to ice bath temperature and quenched with a mixture of 35 mL of acetic acid in 100 mL of water. The organic layer was separated from the aqueous layer, the aqueous layer extracted with ether, and the organic layers were combined

and dried over anhydrous magnesium sulfate. The dried solution was evaporated to an oil using a rotovaporator. The oil was dissolved in methanol and allowed to stand in hopes that crystallization would occur. An oil began to form and was later separated from the mother liquor. The mother liquor was evaporated and redissolved in methanol. This process was repeated until no oil separated and only whitish crystals were obtained, mp 134-136°C (dec). In this manner 0.2 g (0.0006 mol, 2.69%) of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8) were obtained.

c. Preparation of 2,5-Diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (9) From 2,5-Diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14)

The title compound was synthesized from 14 using general procedures for Grignard and phenyllithium reactions with similar ketones.

i. Preparation of 2,5-Diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (9) From 2,5-Diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14) Using Grignard reagent.

Into a 250 mL 3-necked round-bottomed flask equipped with a magnetic stirring bar, a water-cooled reflux condenser, an addition funnel, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 0.76 g (0.03 mol) of magnesium, 10 mL of

freshly dried and distilled diethyl ether, and a few drops of both ethylene dibromide and bromobenzene. After the reaction had started, 3.3 g (0.021 mol) of bromobenzene in 15 mL of the anhydrous diethyl ether was added dropwise to the stirred solution over 30 min. When the addition was complete and the initial reaction had subsided, the reaction mixture was stirred and refluxed for an additional hour, cooled, and 2 mL of dry benzene added. To this stirred solution was added dropwise 2.3 g (0.008 mol) of 2,5-diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14) in 50 mL of dry benzene over 10 min. The red solution was then stirred and refluxed for 1 h during which time the solution became clear yellow. Then the reaction mixture was cooled in an ice bath and quenched with 20 mL of a 10% solution of ammonium chloride in water. The organic and aqueous layers were separated, the aqueous layer extracted with benzene or ether, the organic layers combined, dried over anhydrous magnesium sulfate, and the dried solution evaporated to an oil via a rotovaporator. Attempts at crystallization of the oil were unsuccessful. The product was, however, purified via a 15 cm silica gel column using benzene and petroleum ether as solvents (3:1). A yellow-orange band quickly eluted, was collected and evaporated to an oil using a rotovaporator. Residual solvent was removed by heating gently under vacuum (0.1 mm). In this manner 1.93 g (0.0053 mol, 66%) of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

(9) was obtained in pure form. The pure oil, when exposed to UV-light, fluoresced. Analysis of this oil using IR, C_{13} and ^1H NMR showed peaks that were consistent with the proposed structure. The compound was found to decompose if not kept at freezer temperatures. This made CHN analysis inaccurate.

Anal: Calc'd for $C_{27}H_{26}O$: C, 88.49 ; H, 7.14

found: C, 86.55 ; H, 7.07

MW (Mass spec) Calc'd: 366

found: 366

^1H NMR: (CDl_3, TMS) 6.9-7.5(m,15), 2.2(q,4), 2 (s,1), 0.9(t,6)

IR: ($CHCl_3$) 3660 cm^{-1}

ii. Preparation of 2,5-Diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (9) from 2,5-Diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14) Using Phenyllithium

Into a 100 mL 3-necked microware round-bottomed flask equipped with a magnetic stirring bar, a water-cooled reflux condenser, an addition funnel, and a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen) were placed 1.72 g (0.0058 mol) of 2,5-diethyl-3,4-diphenyl-2,4-cyclopentadien-1-one (14) and 30 mL of freshly dried and distilled diethyl ether. This red solution was stirred, cooled to -10°C by means of an ice-methanol bath, and to it

added dropwise 6.0 mL (0.012 mol) of a 2 molar solution of phenyllithium in diethyl ether and cyclohexane. The solution color changed during the addition from red to purple. The reaction mixture was quenched after being allowed to react for 10 min with 20 mL of a 10% solution of ammonium chloride in water. Upon quenching, the organic layer became yellow. The aqueous and organic layers were separated, the aqueous layer was extracted with ether, the combined organic layers dried over anhydrous magnesium sulfate, and the dried solution evaporated to an oil using a rotovaporator. The oil was purified via a 15 cm silica gel column using benzene and petroleum ether as solvents (3:1). The yellow fraction that eluted was collected, evaporated, and the residual solvent removed under vacuum (0.1 mm) to give 1.7 g (0.0046 mol, 77.7%) of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (9) in pure form. The compound obtained in this way was the same as that obtained from the previous reaction.

The reaction of 14 with phenyllithium at reflux was attempted. In this reaction the ketone 14 was added to an excess of the phenyllithium at ice bath temperature (0°C), and the temperature later raised to reflux the solution. Also, the phenyllithium was prepared in situ and was not a commercial preparation. The reaction gave a mixture of the desired alcohol 9 and a ketone which was assumed to be the

product from the rearrangement of the initially formed anion to ketone.

d. Preparation of 15,16,17-Triphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-ol (11) From 15,16-Diphenylbicyclo [12.2.1]heptadeca-14,16-dien-17-one (16)

The title compound was synthesized from 16 by using general procedures for Grignard and phenyllithium reactions with similar compounds.

i. Preparation of 15,16,17-Triphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-ol (11) From 15,16-Diphenylbicyclo [12.2.1]heptadeca-14,16-dien-17-one (16) Using Grignard Reagent.

Into a 100 mL 3-necked microware round-bottomed flask equipped with a magnetic stirring bar, a water-cooled reflux condenser, an addition funnel, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 0.48 g (0.0196 mol) of magnesium, 5 mL of freshly dried and distilled diethyl ether, and a few drops of both ethylene dibromide and bromobenzene. After the reaction had begun, 2.37 g (0.015 mol) of bromobenzene in 10 mL of the anhydrous diethyl ether was added dropwise over 30 min to the stirred reaction mixture. When the addition was complete and the initial reaction had subsided, the reaction mixture was refluxed for an additional 1.5 h,

decanted into an addition funnel, and saved. Into a similar apparatus as just described were placed 1.5 g (0.0038 mol) of 15,16-diphenylbicyclo[12.2.1]heptadeca-14,16-dien-17-one (16) and 20 mL of the anhydrous diethyl ether. The resulting red solution was cooled to 0°C using an ice-water bath and the Grignard reagent added dropwise. When the addition was complete, the yellow reaction mixture was allowed to react for an additional 20 min before being quenched with 10 mL of a 10% solution of ammonium chloride in water. The organic layer was separated from the aqueous layer, the aqueous layer extracted with diethyl ether, and the organic layers combined, washed with water, and dried over anhydrous sodium sulfate. The dried solution was evaporated to an oil using a rotovaporator, the oil dissolved in a small amount of benzene, and methanol added to initiate precipitation. In the manner 0.583 g (0.0012 mol, 32.2%) of 15,16,17-triphenylbicyclo[12.2.1]-heptadeca-14,16-dien-1-ol (11) was formed. Analytical samples of 11 could be obtained by recrystallization from methanol, mp 128-129.5°C. This compound was found to fluoresce when exposed to UV light. The compound also gave results consistent with its structure when analyzed with IR, C_{13}, and ^{1}H NMR.

Anal: Calc'd for $C_{35}H_{40}O$: C, 88.18 ; H, 8.46
found: C, 88.12 ; H, 8.59

MW (Mass spec) Calc'd: 477
found: 477

^{1}H NMR: ($CDCl_3$, TMS) 6.9-7.5(m, 15), 2.3(dd, 4), 1.9(s,1), 1.4(m, 20)

IR: ($CHCl_3$) 3660 cm^{-1}

ii. Preparation of 15,16,17-Triphenylbicyclo[12.2.1] heptadeca-14,16-dien-17-ol (11) From 15,16-Diphenyl bicyclo[12.2.1]heptadeca-14,16-dien-17-one (16) Using Phenyllithium

Into a 100 mL 3-neck microware round-bottom flask equipped with a magnetic stirring bar, a water-cooled reflux condenser, an addition funnel, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 5 mL of freshly dried and distilled diethyl ether, 0.16 g (0.023 mol) of lithium wire (cut directly into the diethyl ether), and several drops of both ethylene dibromide and bromobenzene. When the reaction had started, 1.78 g (0.0113 mol) of bromobenzene in 10 mL of anhydrous diethyl ether was added dropwise over 30 min to the stirred mixture. After the addition was complete and the initial reaction had subsided, the reaction mixture was refluxed for another 1.5 hours. The phenyllithium was then cooled to room temperature, transferred to an addition funnel, and saved.

Into a similar apparatus as just described was placed 1.5 g (0.0038 mol) of 15,16-diphenylbicyclo[12.2.1]-

heptadeca-14,16-dien-17-one (16), and 10 mL of the anhydrous diethyl ether. The red solution was stirred, cooled to -10°C by means of an ice-methanol bath, and to it added the phenyllithium. During the addition the solution became purple and remained purple until it was quenched with 10 mL of a 10% solution of ammonium chloride in water. The reaction time was 10 min and the color of the organic phase of the quenched reaction mixture was light yellow. The organic layer was separated from the aqueous layer, the aqueous layer extracted with diethyl ether, and the organic layers combined, washed with water, dried over anhydrous sodium sulfate, and the dried solution evaporated to an oil using a rotovaporator. The oil was purified by crystallization using benzene-methanol as solvents. In this manner 1.2 g (0.0025 moles, 66.3%) of 15,16,17-triphenylbicyclo[12.2.1]-heptadeca-14,15-dien-17-ol (11) were obtained, mp 124.5-126.5°C.

It was found that if the above reactions were done at or above room temperature, the product contained none of the expected alcohol. Instead there was obtained from the reaction a mixture of two ketones. Infra-red and ^{1}H NMR analysis of the mixture suggested that the ketones were the conjugated and unconjugated forms of the rearranged products of the initial product from the reaction of 11 with phenyllithium. This seems to be another case of anion rearrangement.

e. Preparation of 2,5-Di(t-butyl)-1,3-diphenyl-2,4-cyclopentadien-1-ol (10) From 2,5-Di(t-butyl-3-phenyl-2,4-cyclpentadiene-1-one(15).

The title compound was prepared from 2,5-di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (15) using general procedures for phenyllithium reactions with similar ketones. Into a 100 mL 3-necked microware round-bottomed flask equipped with a magnetic stirring bar, an air-cooled reflux condenser, an addition funnel, and a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), was placed 0.5 g (0.0019 mol) of 15 in 20 mL of freshly dried and distilled diethyl ether. The orange solution was stirred and cooled to -10°C by means of an ice-methanol bath, and to it added dropwise 2 mL of a 2 M solution of phenyllithium in 30% ether-70% cyclohexane (0.004 mol). The solution became purple as the reagent was added and remained purple until the reaction was quenched after 10 min with 10 mL of a 10% solution of ammonium chloride in water. When the reation mixture was quenched, the organic layer became pale yellow and was separated from the aqueous layer. The aqueous layer was extracted with diethyl ether, the organic layers combined, dried over anhydrous magnesium sulfate, and the dried solution evaporated to an oil using a rotovaporator. The oil was purified by column chromotography on a 15 cm silica gel column using benzene and petroleum ether (3:1) as solvents. A yellow band quickly eluted, was collected,

evaporated to an oil using a rotovaporator, and the residual solvent removed with a vacuum pump (0.1 mm). In this manner 0.587 g (0.0017 mol, 89%) of 2,5-di(t-butyl)-1,3-diphenyl-2,4-cyclopentadien-1-ol (10) was obtained. It was found that if 10 was exposed to UV-light it fluoresced. The purified product also gave results consistent with its structure when analyzed by IR, and C_{13} and ^1H NMR.

Anal: Calc'd for $C_{25}H_{30}O$: C, 86.66 ; H, 8.72

found: C, 86.73 ; H, 8.92

MW (Mass spec) Calc'd: 347

found: 347

^1H NMR: ($CDCl_3$,TMS) 7.2-7.6(m,10), 5.8(s,1), 2.0(s,1), 0.9(s,9), 0.8(s,9)

IR: ($CHCl_3$) 3640 cm^{-1}

It was found that if 15 was reacted with phenylmagnesium bromide at room temperature no alcohol was present in the product. Instead the IR spectrum of the product showed peaks at 1760 and 1710 cm^{-1} indicating ketone functions. It was believed that the ketones were due to the rearrangement of the anion formed by the initial condensation of the phenyllithium and 15.

f. Preparation of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol-(1) From 2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-one (2)

The title compound was prepared using general procedures for Grignard and Phenyllithium reactions.

i. Preparation of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) From 2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-one (2) Using Grignard Reagent.

Into a 250 mL 3-necked round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, an addition funnel, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen) and a heating mantle were placed 1.98 g (0.081 mol) of magnesium, 15 mL of freshly dried and distilled diethyl ether, and a few drops each of bromobenzene and dibromoethane. After the reaction had started, 9.82 g (0.063 mol) of bromobenzene in 25 mL of the anhydrous diethyl ether was added at a rate which allowed gentle reflux. When the addition was complete and the reaction had subsided, the mixture was refluxed for an additional 1.5 hours. At this time the solution was cooled to just above room temperature and to it added 6.06 g (0.016 mol) of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (2) in 100 mL of warm, anhydrous benzene. After the addition was complete the solution was bright yellow and gave no indication that there was unreacted 2 present. Because of this

fact, the solution was not refluxed for the normal 2 h period but instead was quenched by addition of 50 mL of a 10% aqueous ammonium chloride solution. The organic and aqueous layers were separated, the aqueous layer extracted with 50 mL of benzene, the combined organic layers dried over anhydrous magnesium sulfate and the dried solution evaporated to an oil using a rotovaporator. The oil was purified by recrystallization from a benzene/petroleum ether mixture (1:3). The crystals that were obtained from this purification were mostly yellow with a slight purple tint. Because of this the crystals were again recrystallized (as before) to give 5.1 g (0.011 mol, 68.5%) of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1), mp 176-178°C (Lit.[5] 177°C).

ii. Preparation of 1,2,3,4,5-Pentaphenyl-2,4-cyclopendatien-1-one (2) From 2,3,4,5-Tetraphenyl-2,4-cyclopentadien-1-one (2) Using Phenyllithium Reagent

The title compound was prepared using essentially the procedure of Gilman.[26] Into a 250 mL 3-necked round-bottomed flask equipped with a magnetic stirring bar, a water-cooled reflux condenser, an addition funnel, a nitrogen inlet (all of which had been oven-dried and cooled under nitrogen), and a heating mantle were placed 10 mL of freshly dried and distilled diethyl ether, 0.28 g (0.04 mol) of lithium wire (cut directly into the ether), and a few drops of both ethylene

dibromide and bromobenzene. The mixture was stirred, heated gently, and when the reaction had begun, 3.14 g (0.02 mol) of bromobenzene in 15 mL of the anhydrous diethyl ether was added over 30 min. When the addition was complete and the initial reaction had subsided, the reaction mixture was stirred at reflux for an additional hour. After this time 50 mL of dry benzene was added and the reagent was stirred and cooled to 0°C by means of an ice-water bath. To the cooled reagent was added dropwise 3.84 g (0.01 mol) of 2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-one (2) in 100 mL of warm benzene. When the addition was complete, the reaction mixture was quenched with 55 mL of a 10% solution of ammonium chloride in water. The organic phase was yellow and was separated from the aqueous layer, and the aqueous layer extracted with benzene. The combined organic layers were washed with water, dried over anhydrous magnesium sulfate, and the dried solution evaporated to an oil using a rotovaporator. To the oil was added approximately 30 mL of benzene, the solution heated to boiling, and approximately 70 mL of petroleum ether added to the solution. The solution was left to slowly crystallize. In this manner 4.0 g (0.0086 mol, 86.5%) of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) was prepared, mp 175-177°C (Lit.[5] 177°C).

3. Synthetic Methods For The Preparation of Rearranged Ketones.

The ketones were prepared by the thermal rearrangement of the appropriate alcohol. All of the ketones that were prepared in this manner were unknown in the literature except for the 2,2,3,4,5-pentaphenyl-3-cyclopentene-1-one and its conjugated isomer.

a. Preparation of 2,5-Dimethyl-2,3,4-triphenyl-3-cyclopenten-1-one (33) From 2,5-Dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8) Via Thermal Isomerization.

Into a 100 mL 3-necked microware round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, a glass stopper, a nitrogen inlet (all of whch had been acid-washed, oven-dried, and cooled under nitrogen), a serum sleeve, and a heating mantle were placed 30 mL of decane and 1.5 g (0.0044 mol) of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8). The solution was stirred and heated at reflux (174^{o}C) under nitrogen for 32 hours. At this time the solution was cooled to room temperature and allowed to slowly crystallize. When no crystals had formed after 12 h, the solution was cooled in a freezer. The solid which had formed was filtered and collected. Other fractions of the compound were obtained by evaporating the solvent, cooling, and filtering the product. In this manner 0.7 g of 2,5-dimethyl-2,3,4-triphenyl-3-cyclopenten-1-one

(33) was obtained. The remaining solution was later heated under vacuum to remove the remaining solvent. When all the solvent was removed an additional 0.4 g of 33 were obtained. The total yield of 33 was 1.1 g (0.0033 mol, 74%). Analytical samples of 33 were obtained by recrystallization from methanol, mp 113-115°C. This compound was found to fluoresce upon exposure to UV light. The compound also gave results consistent with its structure when analyzed with IR, C_{13}, and ^1H NMR.

Anal: Calc'd for $C_{25}H_{22}O$: C, 88.72; H, 6.55

found: C, 88.6 ; H, 6.5

MW (Mass spec) Calc'd: 338

found: 338

^1H NMR: ($CDCl_3$,TMS) 6.8-7.6(m,15), 3.7(q,1), 1.5(s,3), 1.2(d,3)

IR: ($CHCl_3$) 1760 cm^{-1}

b. Preparation of 2,5-Diethyl-2,3,4-triphenyl-3-cyclopenten-1-one (34) From 2,5-Diethyl-1,3-4-triphenyl-2,4-cyclopentadien-1-ol (9) Via Thermal Isomerization.

Into a 50 mL 3-necked microware round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, a glass stopper, a nitrogen inlet (all of which had been acid-washed, oven-dried, and cooled under nitrogen) a serum sleeve, and heating mantle was placed 1.4 g (0.0038

mol) of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (9) in 12 mL of decane. The solution was stirred and heated at reflux (174°C) under nitrogen for 22 hours. At this time the solution was cooled to room temperature and allowed to crystallize. Crystals soon formed and were filtered to yield 0.99 g of 2,5-diethyl-2,3,4-triphenyl-3-cyclopenten-1-one (34). The solution was further cooled in a freezer, and later the decane was removed by distillation to obtain an additional 0.3 g of 34. In this manner a total of 1.3 g (0.0036 mol, 92.9%) of 34 was obtained. Analytical samples of 34, mp 144.5-146.5°C were obtained by repetitive recrystallization of the product from isopropanol. This compound was found to flouresce when exposed to UV light. The compound also gave results consistent with its structure when analyzed by IR, C_{13}, and ^1H NMR.

Anal: Calc'd for $C_{27}H_{26}O$: C, 88.49; H, 7.14

found: C, 88.61; H, 7.25

MW (Mass spec) Cal'd: 366

found: 366

^1H NMR: ($CDCl_3$,TMS) 6.8-7.5 (m,15), 3.6(dd,1), 2.6(q,2), 1.9(dq,2), 1.0(dt,6)

IR: ($CHCl_3$) 1760 cm^{-1}

c. Preparation of 1,15,16-Triphenylbicyclo[12.2.1] heptadeca-15-en-17-one (35) From 15,16,17-Triphenylbicyclo[12.2.1]heptadeca-15-16-dien-17-ol (11) Via Thermal Isomerization.

Into a 100 mL 3-necked microware round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, a glass stopper, a nitrogen inlet (all of which had been acid-washed, oven-dried, and cooled under nitrogen), a serum sleeve, and a heating mantle were placed 20 mL of decane and 1 g (0.0021 mol) 15,16,17-triphenylbicyclo [12.2.1]heptadeca-14,16-dien-17-ol (11). The solution was stirred and heated at reflux (bp 174^{o}C) under nitrogen for 3 hours. At that time the solution was cooled, approximately 10 mL of decane was removed by distillation, and 10 mL of petroleum ether was added to the solution. The solution was then cooled in a freezer and allowed to precipitate. The product that precipitated was filtered to obtain 0.61 g of 1,15,16-triphenylbicyclo[12.2.1]hetadeca-15-en-17-one (35). The remaining solution was further evaporated and cooled in order to obtain an additional 0.14 g of 35. The total yield of 35 was 0.75 g (0.00158 mol, 75%). Analytical samples of 35 were obtained by recrystallization from methanol, mp 95.5-97.2. The compound was found to fluoresce when exposed to UV light and the compound also gave results consistent with its structure when analyzed with IR, $C_{,13}$, and ^{1}H NMR.

Anal: Calc'd for $C_{35}H_{40}O$: C, 88.15; H, 8.56

found: C, 88.19; H, 8.45

MW (Mass spec) Cal'd: 476

found: 476

^1H NMR: (CDl_3, TMS) 6.9-7.5 (m,15), 3.6(dd,1), 2.5(m,2), 2.0(m,2) 1.4(m,20)

IR: ($CHCl_3$) 1760 cm^{-1}

d. Preparation of 2,5-Di(t-butyl)-2,3-diphenyl-3-cyclopenten-1-one (36) From 2,5-Di(t-butyl) 1,3-diphenyl-2,4-cyclopentadien-1-ol (10) Via Thermal Isomerization.

Into a 500 mL 3-necked round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, a ground glass stopper, a nitrogen inlet (all of which had been acid-washed, oven-dried, and cooled under nitrogen), a serum sleeve, and a heating mantle were placed 13 mL of decane and 0.5 g (0.0014 mol) of 2,5-di(t-butyl)-1,3-diphenyl-2,4-cyclopentadien-1-ol (10). The solution was stirred at reflux (bp 174°C) under nitrogen for 196 hours. After this time the reaction was cooled to room temperature and allowed to stand in hope that crystals might form. When crystallization did not occur, the solution was transferred to a distillation flask and the decane removed by vacuum distillation. The red residue from the distillation was analyzed using IR. The spectrum showed strong signals that were characteristic of ketones at 1760 and 1720 cm^{-1}.

Attempts to purify this compound to acceptable purity using recrystallization and column chromotagraphy were not successful; however, a slightly more pure oil was obtained. The IR spectrum of this oil showed the same major peaks as did the other ketones. The ^{1}H NMR spectra showed that the rearrangement of the phenyl group had caused the methyl groups of the ketones to be unequivalent. A mass spectrum of the oil indicated that the product had the correct molecular weight, and no further work was done on this ketone.

e. Preparation of 2,2,3,4,5-Pentaphenyl-3-cyclopenten-1-one (4) From 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) Via Thermal Isomerization.

The title compound was prepared using essentially the procedure of Youssef.[3] Into a 50 mL 3-necked microware round-bottomed flask equipped with a stirring bar, a water-cooled reflux condenser, a ground glass stopper, a nitrogen inlet (all of which had been acid-washed, oven-dried, and cooled under nitrogen), a serum sleeve, and a heating mantle were placed 1.0 g (0.00211 mol) of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol (1) and 20 mL of decane. The solution was stirred and heated at reflux (bp 174°C) under nitrogen for 12 hours. After 12 h the solution was cooled and crystals soon formed. The initially formed crystals were filtered and dried (0.56 g). The filtrate was saved and allowed to stand in a freezer. Additional crystals

formed (0.19 g) and were combined with those previously obtained to give a total of 0.86 g (0.00160 mol, 86%). Analysis of the crystals showed that there was a mixture of unconjugated ketone contaminated with a small amount of the conjugated ketone. The two were separated by column chromatography using a 20 cm silica gel column and carbon tetrachloride as solvent. The unconjugated ketone obtained from the column was recrystalized from benzene and petroleum ether (113) to obtain an analytical sample, mp 190-192: (Lit.[5] 196-197°C).

5. Kinetic Rearrangements of The Alcohols

In general, the alcohols were rearranged thermally at different temperatures using diphenyl ether as solvent (bp 259°C). The parent alcohol 1 was rearranged at 150°, 160°, 170°, 185°, and 200°C; the dimethyl alcohol 8 was rearranged at 170°, 185°, and 200°C; the cyclic alcohol 11 at 150°, 160°, and 170°C and the diethyl alcohol 9 at 170°, 185°, and 200°C. The analytical method used was lc using a Molecular Separation HPLC with an Instramentation Specialties Co. UV detector. Rate constants for the reaction were obtained using a logarithm plot of the percent alcohol remaining versus time. The slope of the line was equal to the rate constant divided by 2.303. The percent alcohol remaining was obtained using a calibration curve constructed by plotting known amounts of alcohol versus its actual area. After the

solutions were prepared two or three 1 ul injections of the samples at each concentration were made into the lc, and the areas obtained averaged. Once the calibration curves of the alcohols were obtained, the kinetic studies were performed in the following manner.

Into a 100 mL 3-necked microware round-bottomed flask equipped with a stirring bar, water-cooled reflux condenser (all of which had been cleaned thoroughly, acid-washed, oven-dried, and cooled under nitrogen) a nitrogen inlet, an extended range thermometer, and heating tape was placed 80 mL of diphenyl ether. The solvent was heated to the desired temperature under nitrogen using an Instruments for Research and Industry Thermowatch coupled to the heating tape. The temperature normally varied from 0.5 to 0.8^{o}C above or below the set temperature due to the heating cycles. After the desired temperature was obtained and had stabalized, 0.6 g of alcohol was added all at once to the solution and the stop watch started. The flask was then equipped with a serum sleeve which allowed samples to be taken without further disturbing the system. At different times during the rearrangement 0.3-0.5 mL samples of the solution were taken and the time noted. After all samples for each kinetic run were obtained, they were analyzed by lc as previously described.

IV. Results

The kinetic data for the rearrangement of the studied alcohols is listed in this section. The data are presented in tabular form in Table I. The data was evaluated by various techniques which are represented by the figures which follow. The rates for the rearrangements were obtained by plotting the log of alcohol remaining versus time. The Arrhenius activation energies were obtained from a plot of log k versus 1/T. Enthalpies of activation were obtained from a plot of log (k/T) versus 1/T. The entropy of activation was obtained from the following equation.

$$\frac{\Delta S^{\neq}}{4.576} = \log k - 10.753 - \log T + \frac{E_a}{4.576\ (T)}$$

The value for the thermodynamic parameters are collectively listed in the discussion. Sample calculations for these parameters are shown in Appendix 1.

Because of problems with introduction of the 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol into the solvent, two methods of data evaluation were used for this compound. The first method was to include all points given in Table I to calculate rate constants while the second method eliminated the zero point. Conclusions and discussion were based on data from method 1 because it allowed better comparison with earlier work and because it placed greater value on the zero point.

Table I

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) at 150 ± 0.5°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100	2.0
2	11,100	84.5	1.93
3	21,900	79.8	1.90
4	44,160	72	1.86
5	61,080	62.7	1.80
6	75,600	55.1	1.74
7	94,680	52.3	1.72
8	108,120	46.7	1.67

$k = 6.59 \times 10^{-6}$

corr = -0.991

$y_{int} = 1.98$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) at 160 ± 0.5°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.0
2	13,860	77.3	1.89
3	20,820	66.2	1.82
4	30,300	55.7	1.75
5	44,400	44.5	1.65
6	54,000	39.5	1.60

$k = 1.73 \times 10^{-5}$

corr = -0.996

$y_{int} = 1.99$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) at 170 ± 0.5°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.0
2	3,660	87.3	1.94
3	10,260	72.3	1.86
4	16,860	58.3	1.76
5	22,860	47.9	1.68
6	31,320	31.9	1.50

$k = 3.55 \times 10^{-5}$

corr = 0.995

$y_{int} = 2.01$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) at 185 ± 0.5°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.0
2	1,800	84.8	1.92
3	3,600	66.2	1.82
4	5,400	52.9	1.72
5	7,200	46.5	1.67
6	9,960	39.0	1.59
7	10,800	28.3	1.45
8	12,600	20.8	1.32

$k = 1.19 \times 10^{-4}$

corr = -0.993

$y_{int} = 2.01$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol (1) at 200 ± 0.6°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.0
2	305	80.4	1.9
3	896	65.2	1.81
4	2,716	31.7	1.50
5	3,298	28.4	1.45
6	4,234	19.3	1.28

$k = 3.77 \times 10^{-4}$

corr = -0.997

$y_{int} = 1.97$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 15,16,17-Triphenylbicyclo-[12.2.1]heptadeca-14,16-dien-17-ol (11) at 150 ± 0.5°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.0
2	1,690	80.1	1.9
3	5,036	47.1	1.67
4	6,725	34.0	1.53
5	8,400	27.4	1.44
6	10,075	20.2	1.31

$k = 1.59 \times 10^{-4}$

corr = -0.99

$y_{int} = 2.01$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 15,16,17-Triphenylbicyclo-[12.2.1]heptadeca-14,16-dien-17-ol (11) at 160 ± 0.6°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.0
2	838	75.6	1.88
3	2,516	43.9	1.64
4	3,357	32.1	1.51
5	4,205	23.4	1.37
6	5,031	16.8	1.23

$k = 3.5 \times 10^{-4}$

corr = -0.999

$y_{int} = 2.01$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 15,16,17-Triphenylbicyclo-[12.2.1]heptadeca-14,16-dien-17-ol (11) at 170 ± 0.5°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.0
2	895	54.0	1.73
3	1,320	38.5	1.59
4	1,729	27.5	1.44
5	2,210	18.2	1.26
6	2,574	12.9	1.11

$k = 7.96 \times 10^{-4}$

corr = -0.998

$y_{int} = 2.02$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 2,5-Diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (9) at 170 ± 0.6°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.00
2	10,799	57.8	1.76
3	16,232	50.0	1.70
4	20,728	42.2	1.62
5	26,593	34.5	1.54

$k = 3.95 \times 10^{-5}$

corr = -0.992

$y_{int} = 1.98$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 2,5-Diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (9) at 185 ± 0.6°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.00
2	1,792	86.6	1.93
3	3,595	67.7	1.83
4	7,197	41.2	1.61
5	9,036	36.0	1.56

$k = 1.18 \times 10^{-4}$

corr = -0.995

$y_{int} = 2.01$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 2,5-Diethyl-1,3,4-triphenyl-2-4-cyclopentadien-1-ol (9) at 200 ± 0.8°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.00
2	1,202	73.1	1.86
3	1,806	53.9	1.73
4	2,403	45.0	1.65
5	3,002	35.3	1.55

$k = 3.5 \times 10^{-4}$

corr = -0.995

$y_{int} = 2.01$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 2,5-Dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol (8) at 170 ± 0.6°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.00
2	16,792	56.7	1.75
3	21,600	52.5	1.72
4	23,140	50.8	1.71
5	33,610	42.3	1.63

$k = 2.58 \times 10^{-5}$

corr = -0.98

$y_{int} = 1.98$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 2,5-Dimethyl-1,3,4-triphenyl-2-4-cyclopentadien-1-ol (8) at 185 ± 0.6°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.00
2	3,594	61.8	1.79
3	5,405	55.0	1.74
4	7,197	50.0	1.70

$k = 9.7 \times 10^{-5}$

corr = -0.98

$y_{int} = 1.98$

Table I

(Continued)

Kinetic Data For All Alcohol Rearrangements

The Isomerization of 2,5-Dimethyl-1,3,4-triphenyl-2-4-cyclopentadien-1-ol (8) at 200 ± 0.8°C

Sample Number	Time Sec.	% Conc	Log % Conc
1	0	100.0	2.00
2	1,202	59.3	1.77
3	1,812	53.0	1.72
4	2,404	48.6	1.68
5	3,002	43.0	1.62

$k = 2.7 \times 10^{-4}$

corr = -0.97

$y_{int} = 1.96$

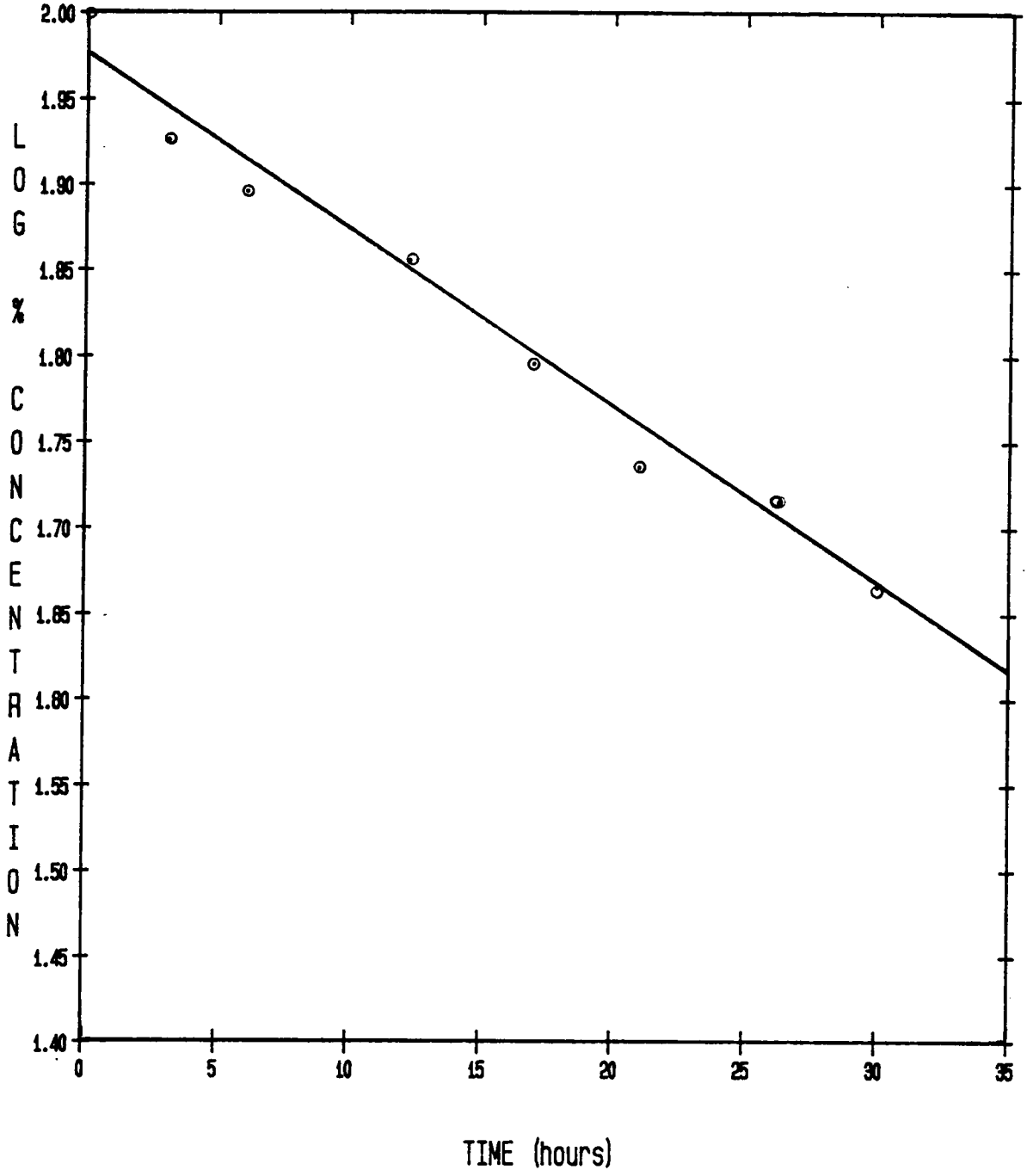


Fig. 1. Variation with time of the logarithm of the concentration of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol at 150 $\pm$ 0.5°C

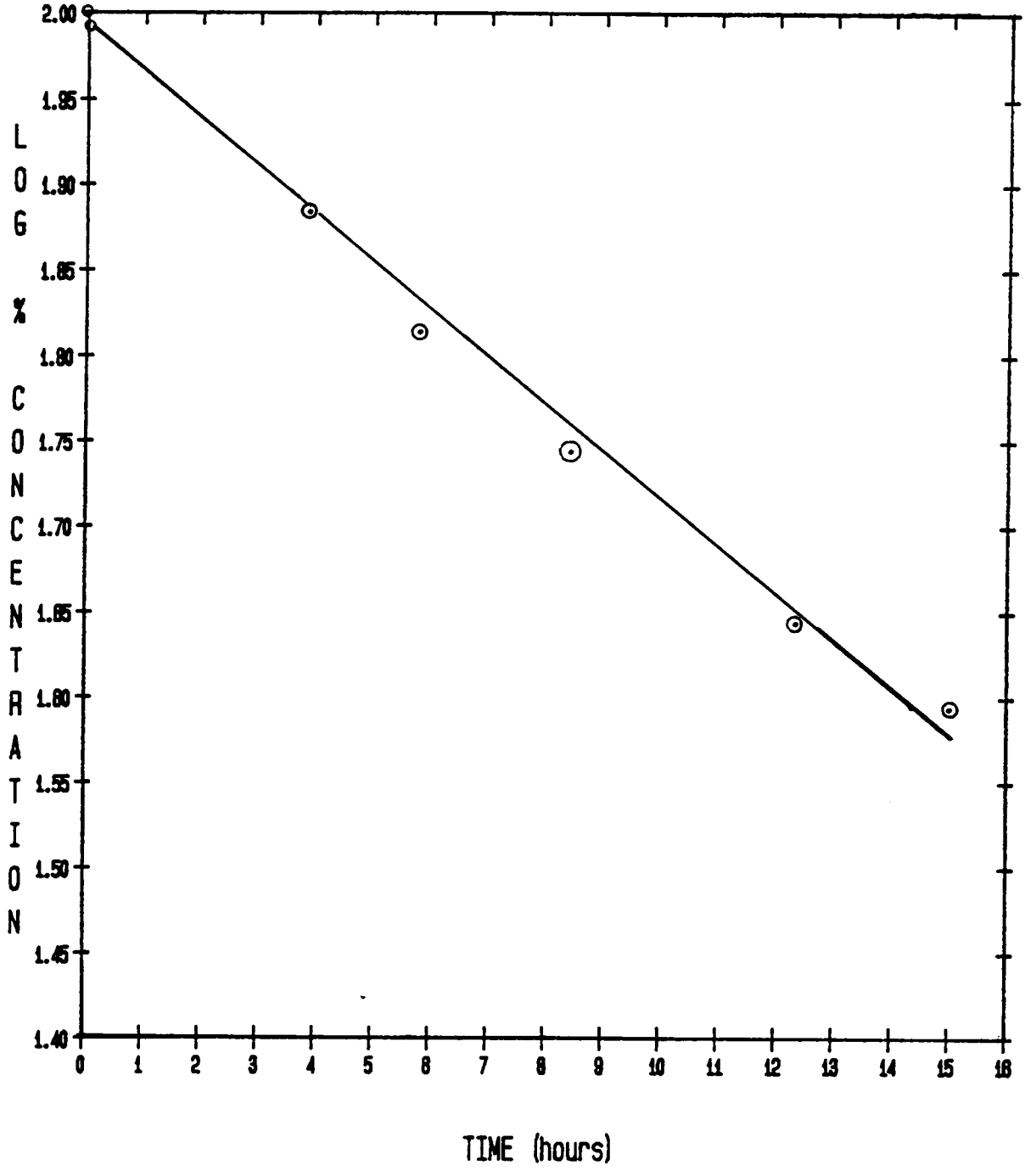


Fig. 2. Variation with time of the logarithm of the concentration of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol at 160 $\pm$ 0.5°C

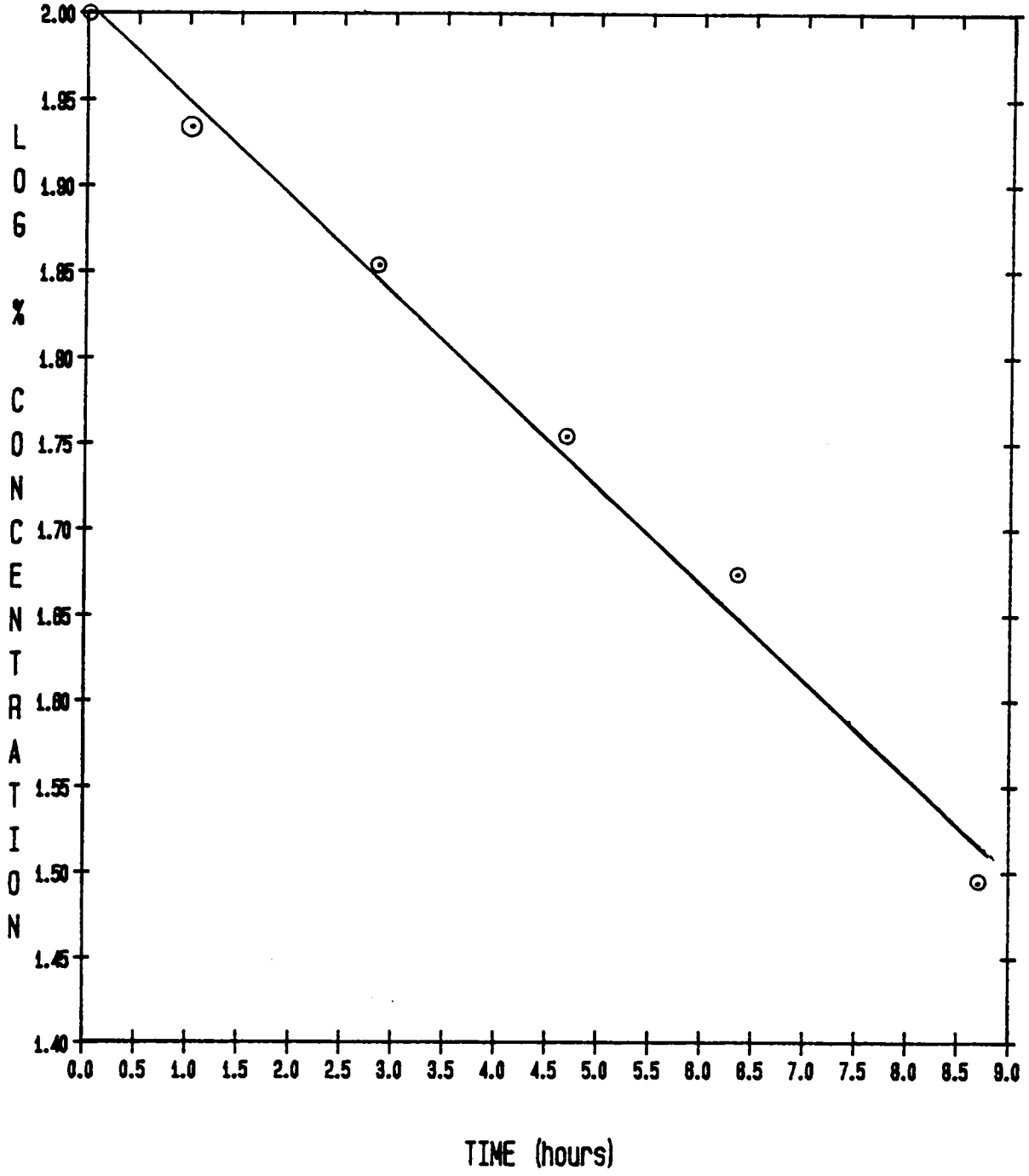


Fig. 3. Variation with time of the logarithm of the concentration of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol at 170 $\pm$ 0.5°C

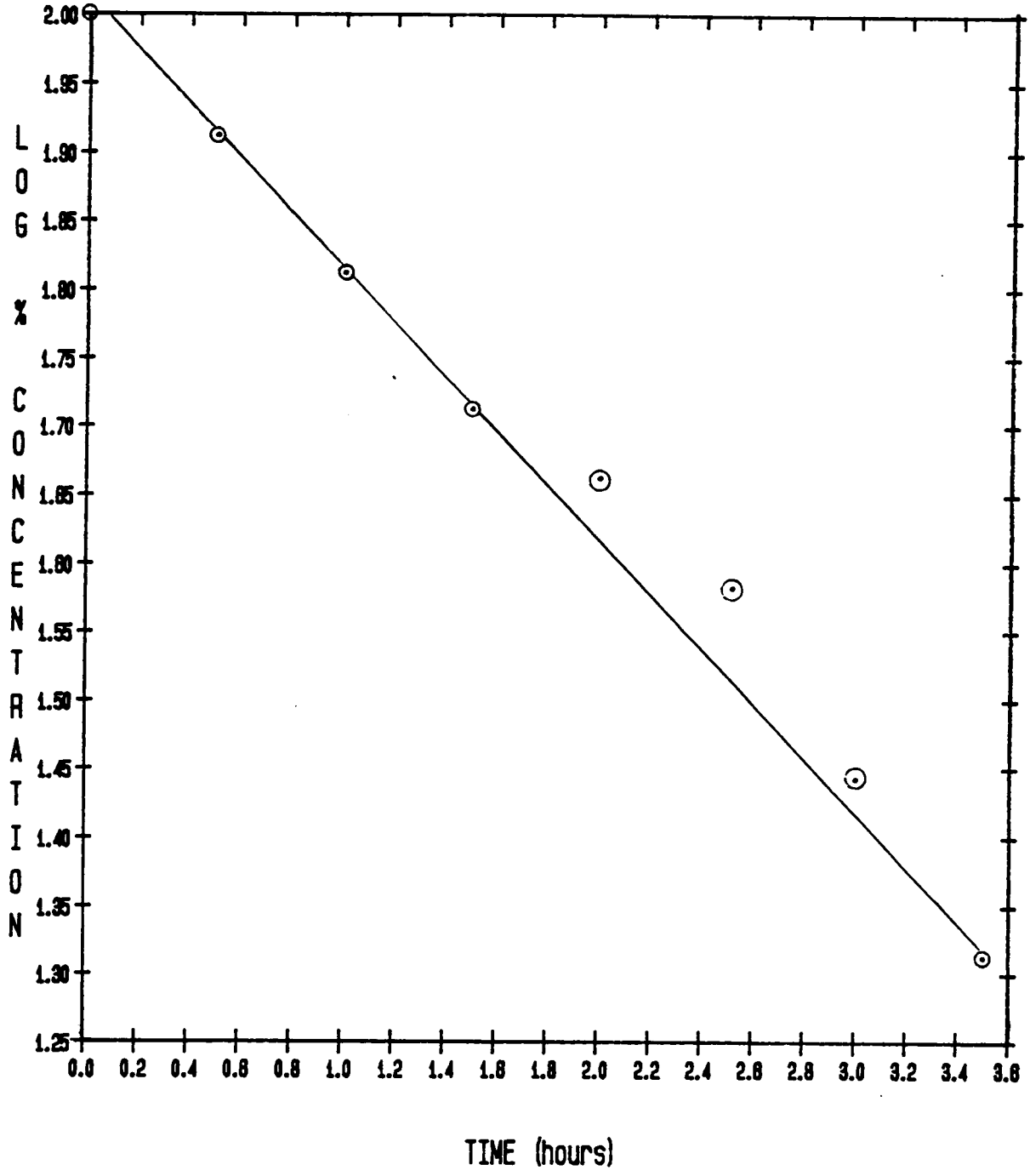


Fig. 4. Variation with time of the logarithm of the concentration of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol at 185 $\pm$ 0.6°C

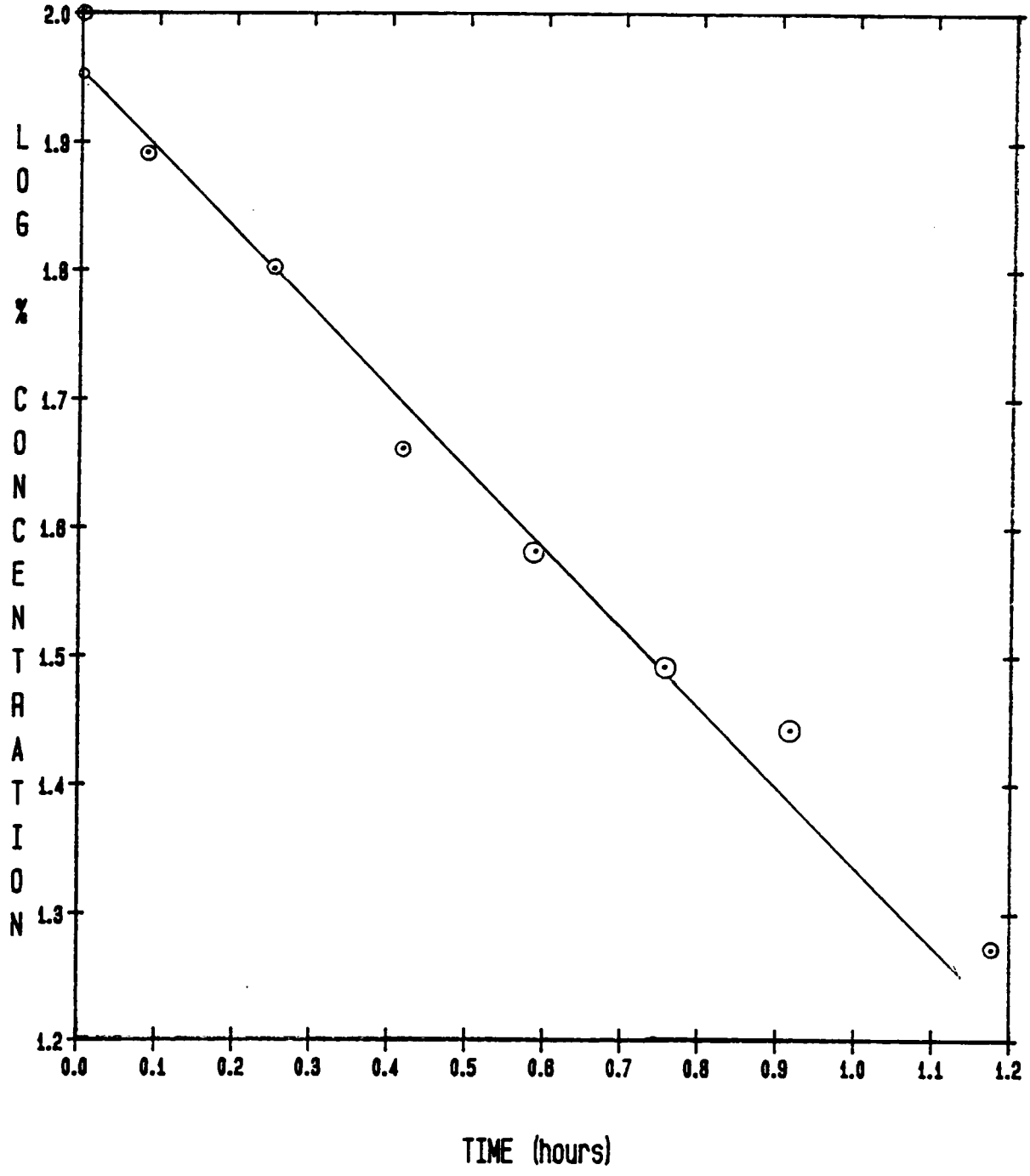


Fig. 5. Variation with time of the logarithm of the concentration of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol at 200 $\pm$ 0.6°C

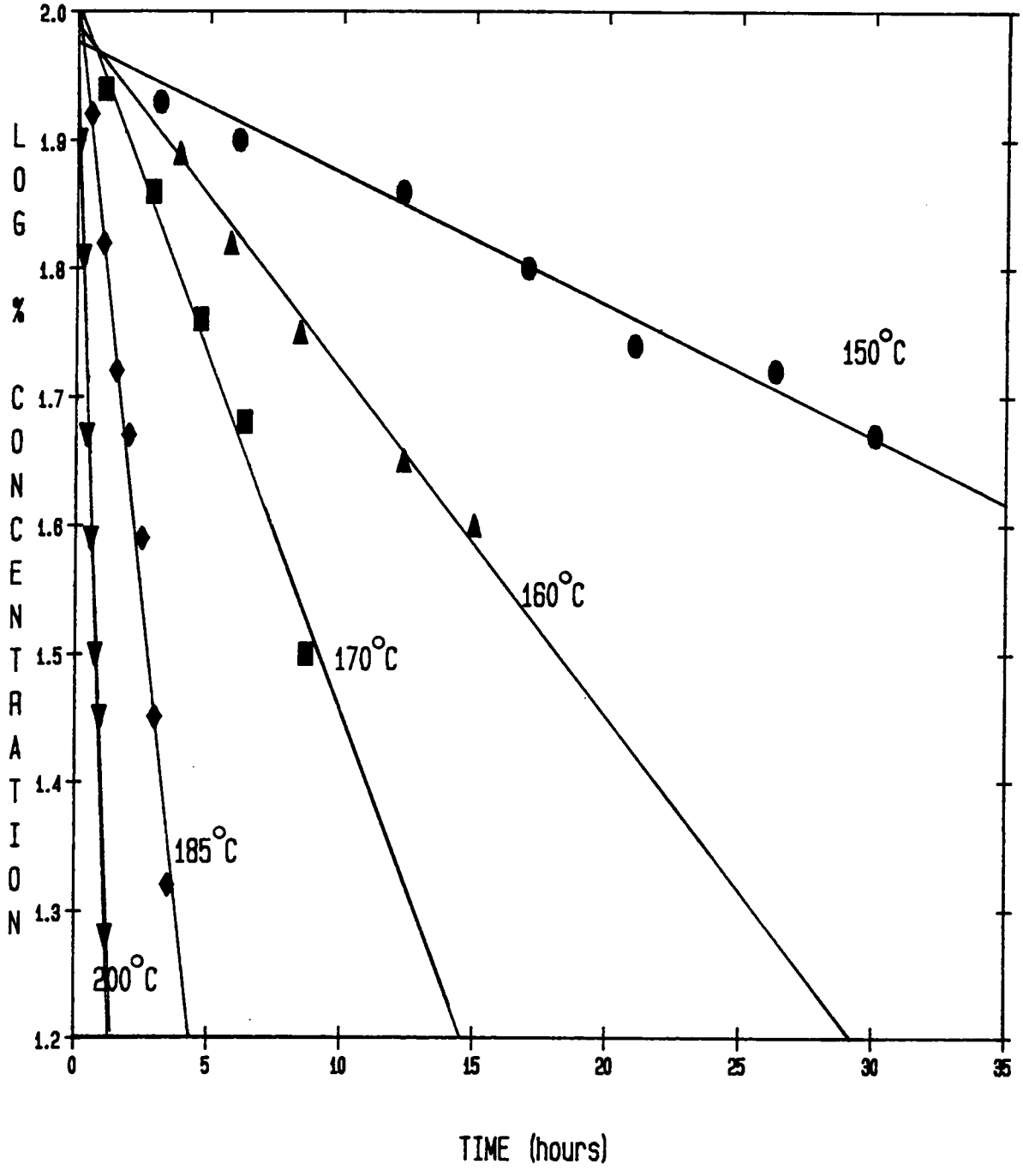


Fig. 6. Variation with time of the logarithm of the concentration of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol over the temperature range of 150-200° C

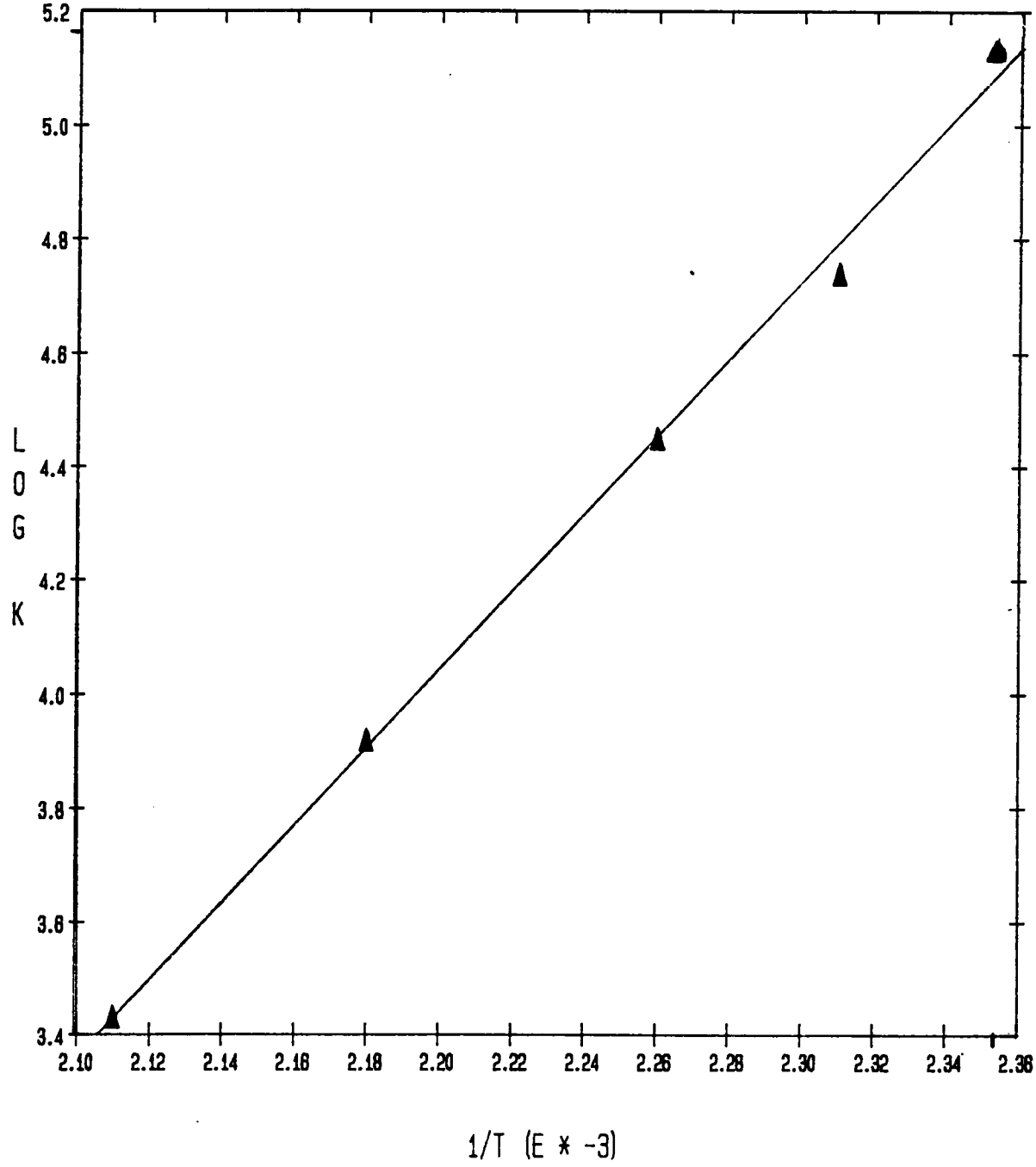


Fig. 7. Variation of Log k versus 1/T over the temperature range of 150-200 ± 0.5°C for the evaluation of E_a of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol

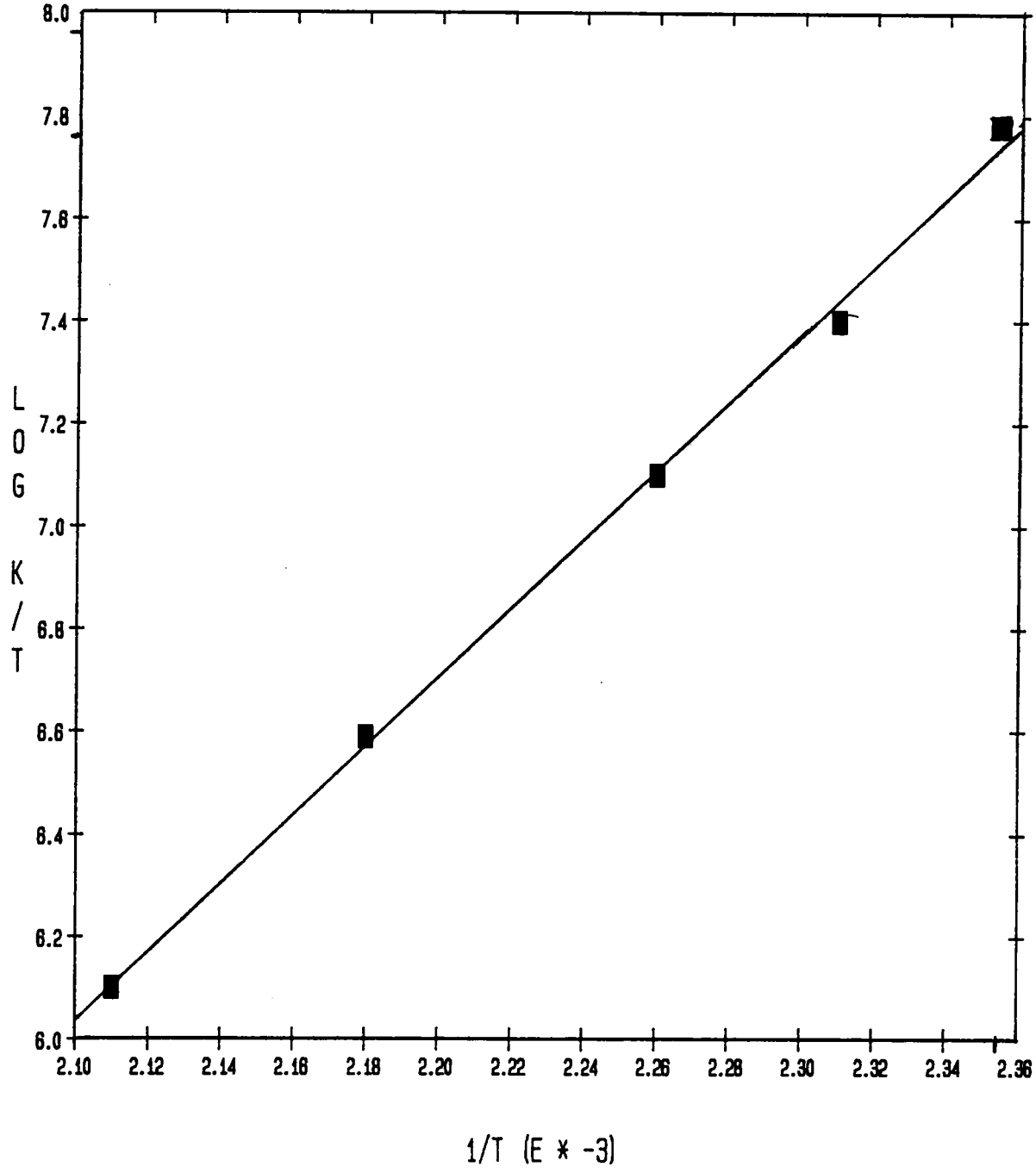


Fig. 8. Variation of Log (k/T) versus 1/T over the temperature range of 150-200° ± 0.5°C for the evaluation of ΔH of 1,2,3,4,5-pentaphenyl-2,4,-cyclopentadien-1-ol

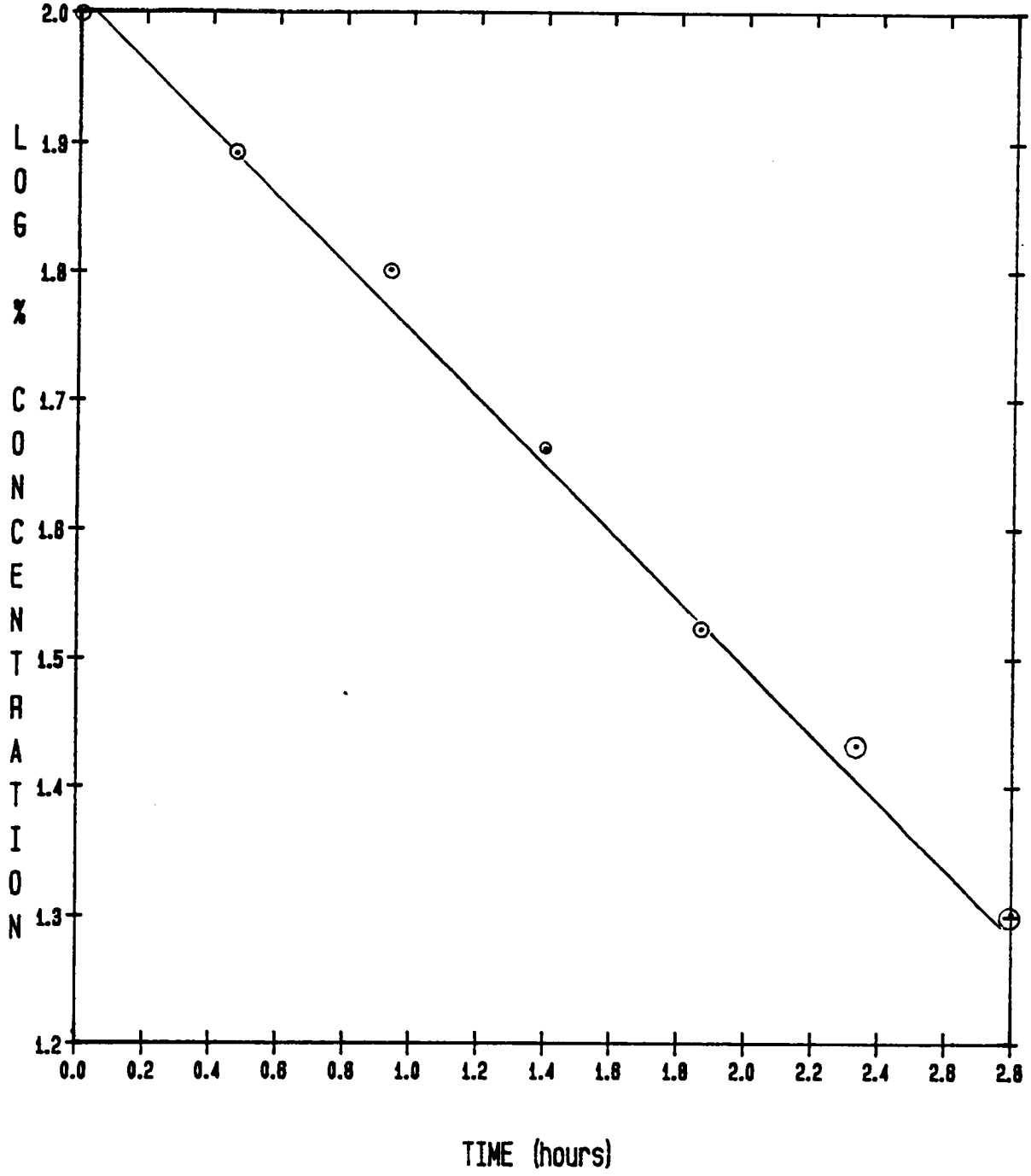


Fig. 9. Variation with time of the logarithm of the concentration of 15,16,17-triphenylbicyclo-[12.2.1]heptadeca-14,16-dien-17-ol at 150 ± 0.6°C

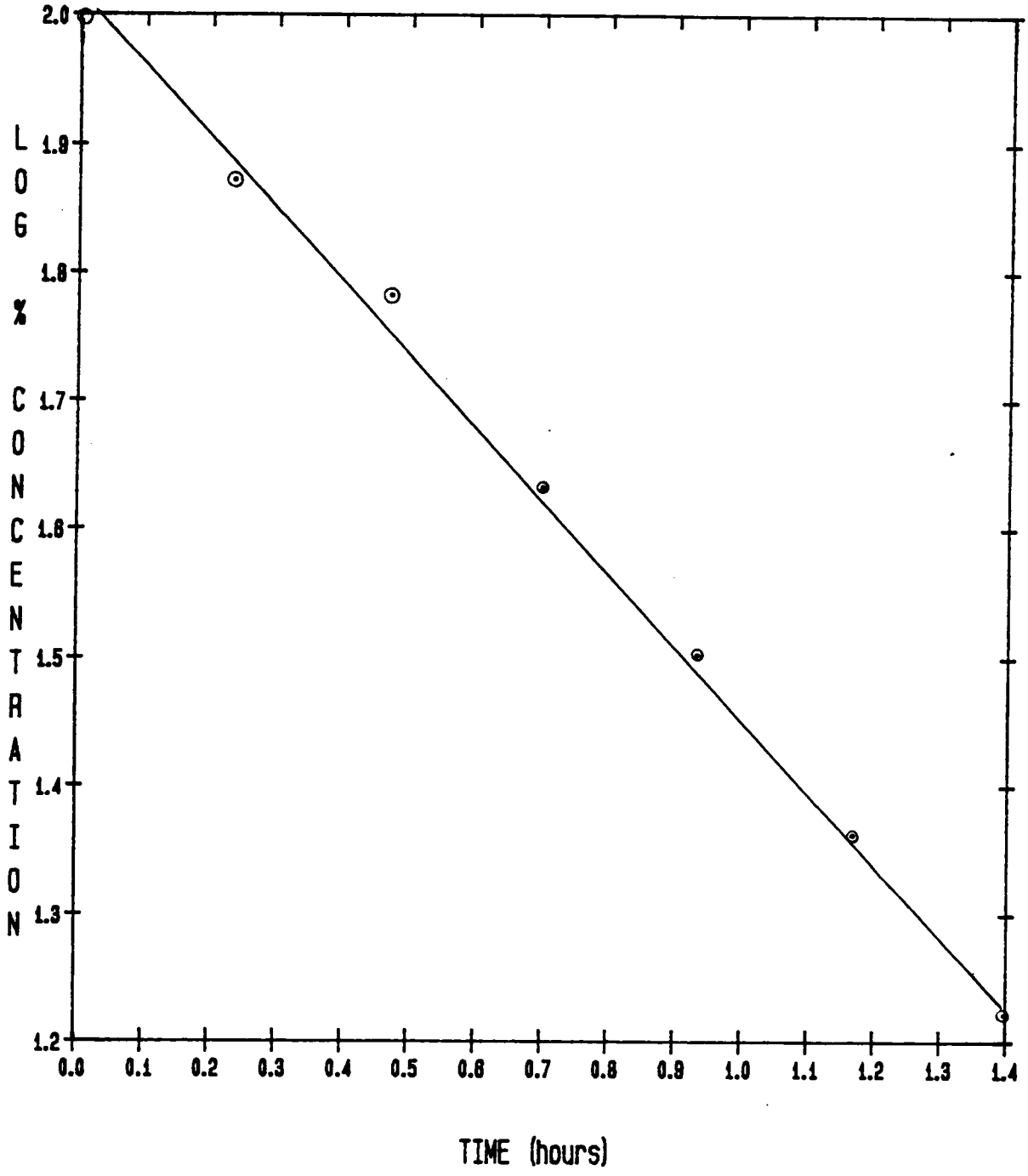


Fig. 10. Variation with time of the logarithm of the concentration of 15,16,17-triphenylbicyclo-[12.2.1]heptadeca-14,16-dien-17-ol at 160 ± 0.7°C

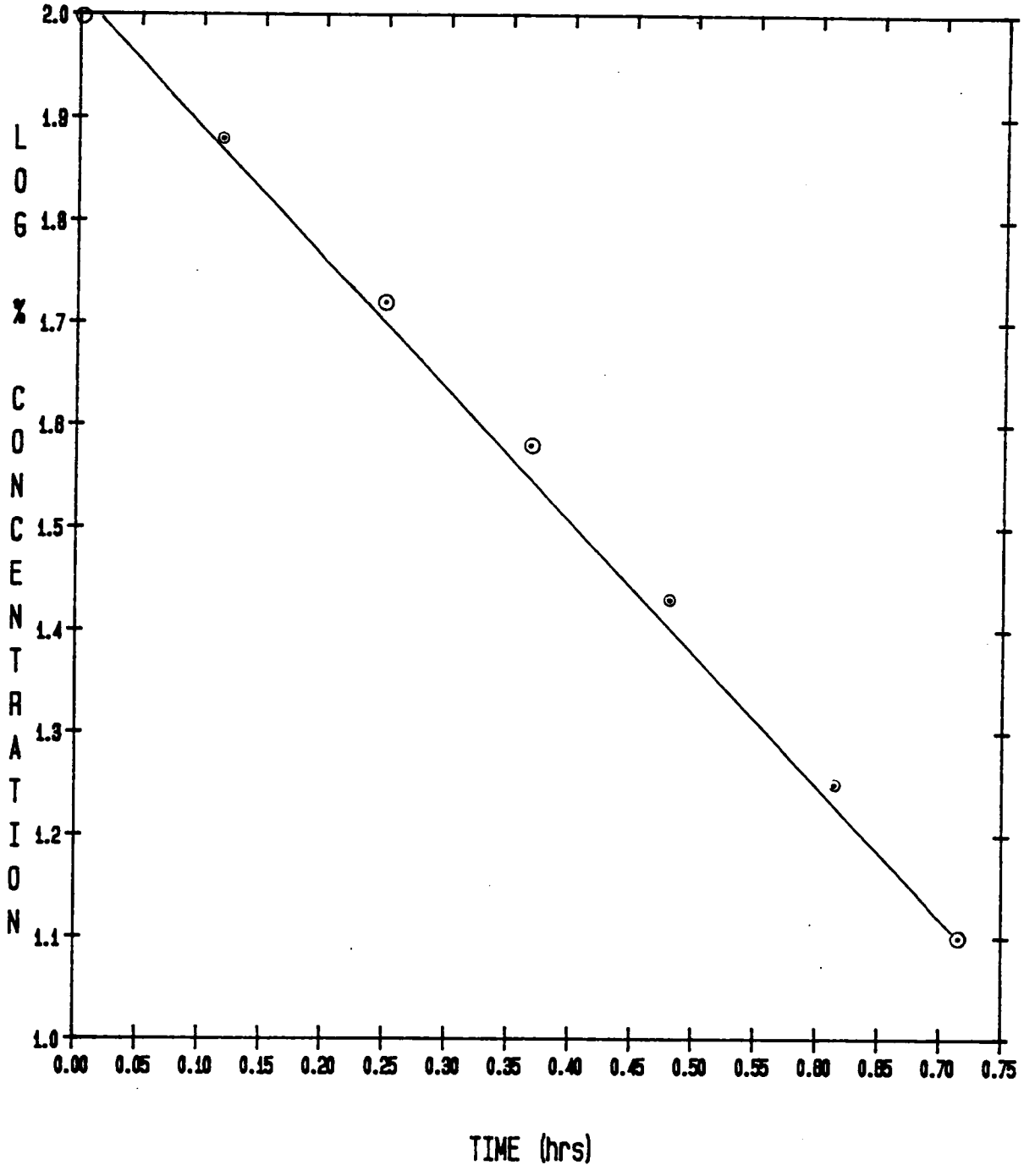


Fig. 11. Variation with time of the logarithm of the concentration of 15,16,17-triphenylbicyclo-[12.2.1]heptadeca-14,16-dien-17-ol at 170 ± 0.5°C

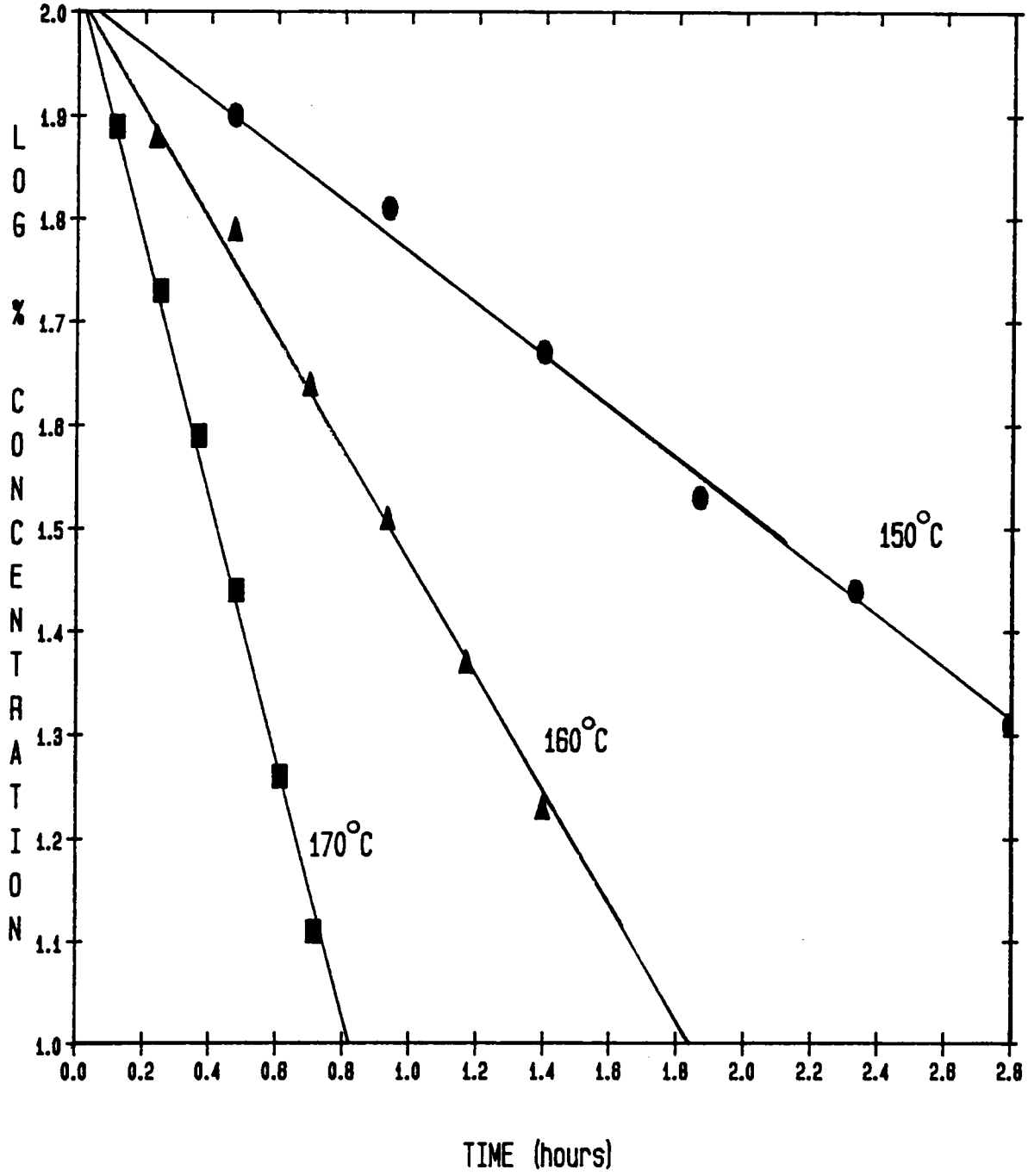


Fig. 12. Variation with time of the logarithm of the concentration of 15,16,17-triphenylbicyclo-[12.2.1]heptadeca-14,16-dien-17-ol over the temperature range of 150-170°C

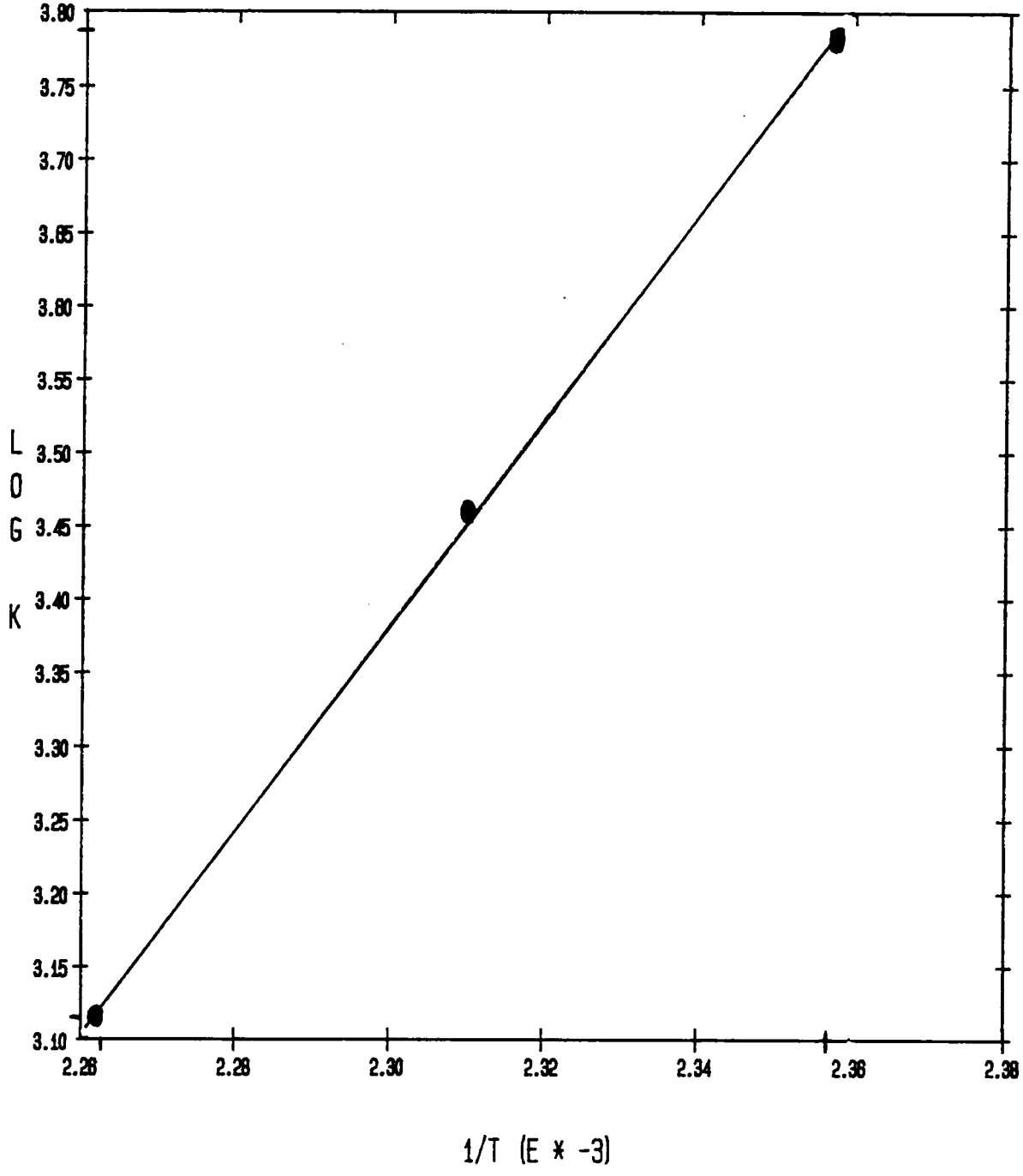


Fig. 13. Variation of Log k versus 1/T over the temperature range of 150-170 ± 0.5°C for the evaluation of E_a of 15,16,17-triphenyl-bicyclo[12.2.1]heptadeca-14,16-dien-17-ol

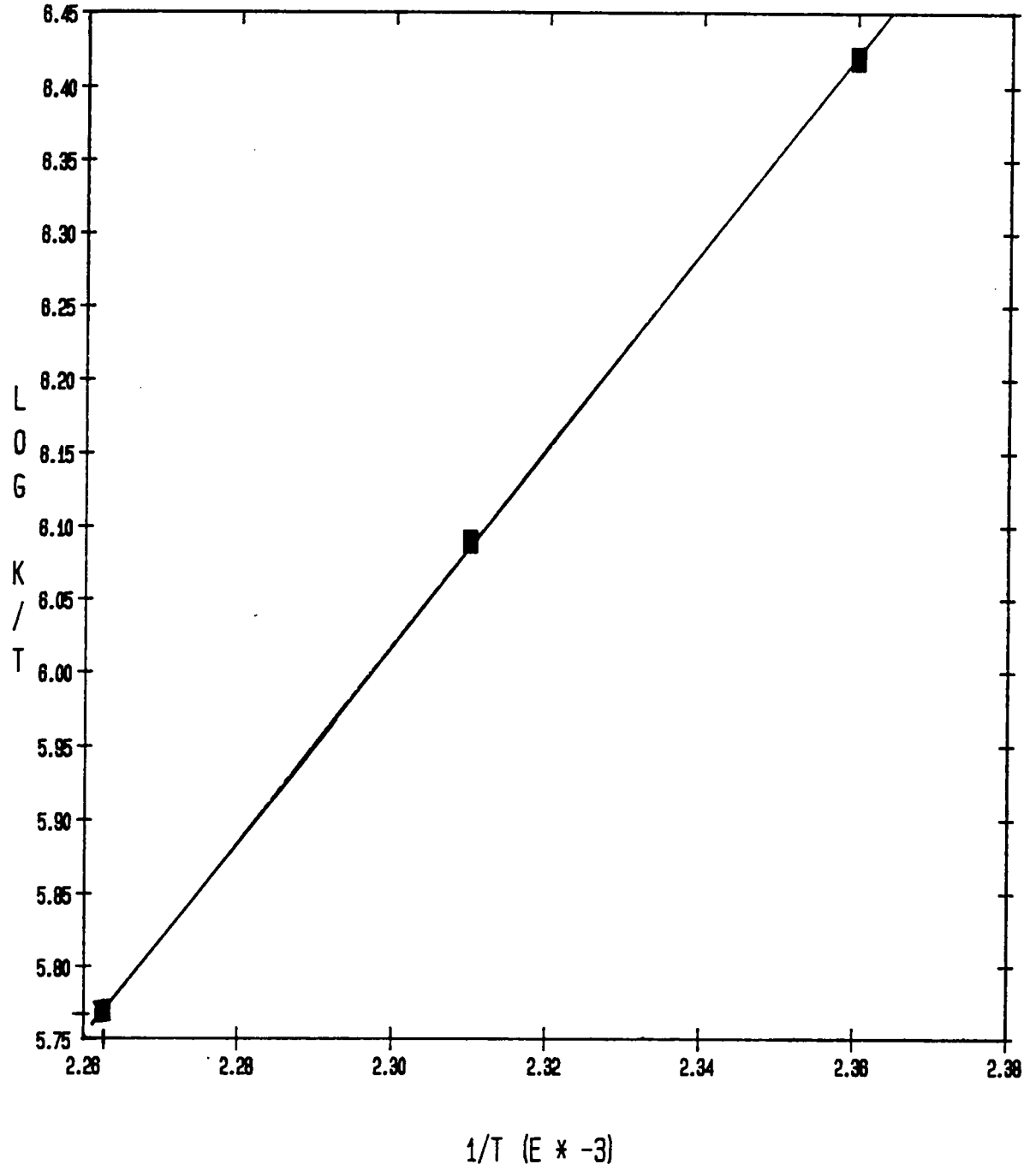


Fig. 14. Variation of Log (k/T) versus 1/T over the temperature range of 150-170 ± 0.5°C for the evaluation of ΔH of 15,16,17-triphenyl-bicyclo[12.2.1]heptadeca-14,16-dien-17-ol

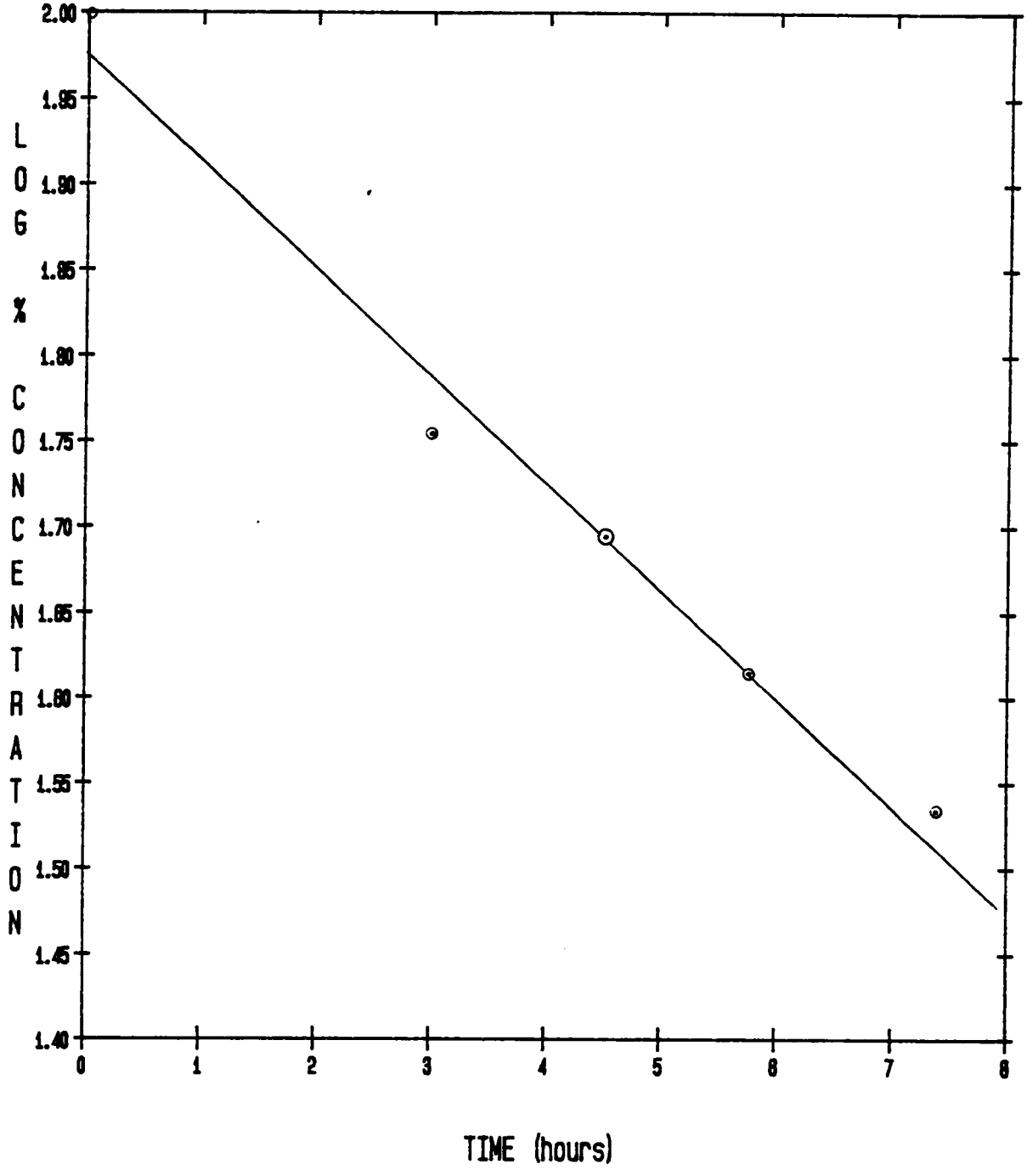


Fig. 15. Variation with time of the logarithm of the concentration of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 170 ± 0.6°C

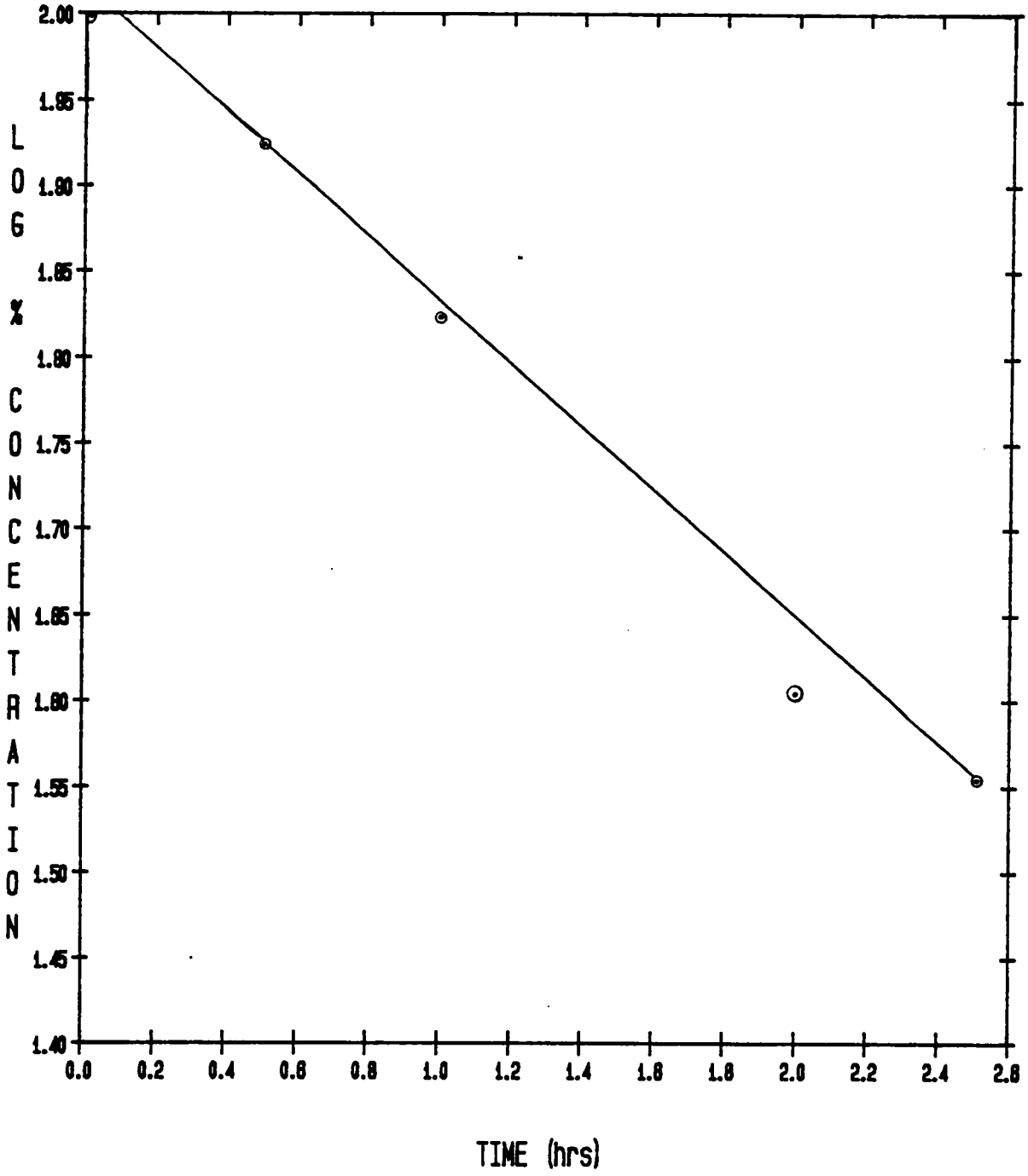


Fig. 16. Variation with time of the logarithm of the concentration of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 185 $\pm$ 0.6°C

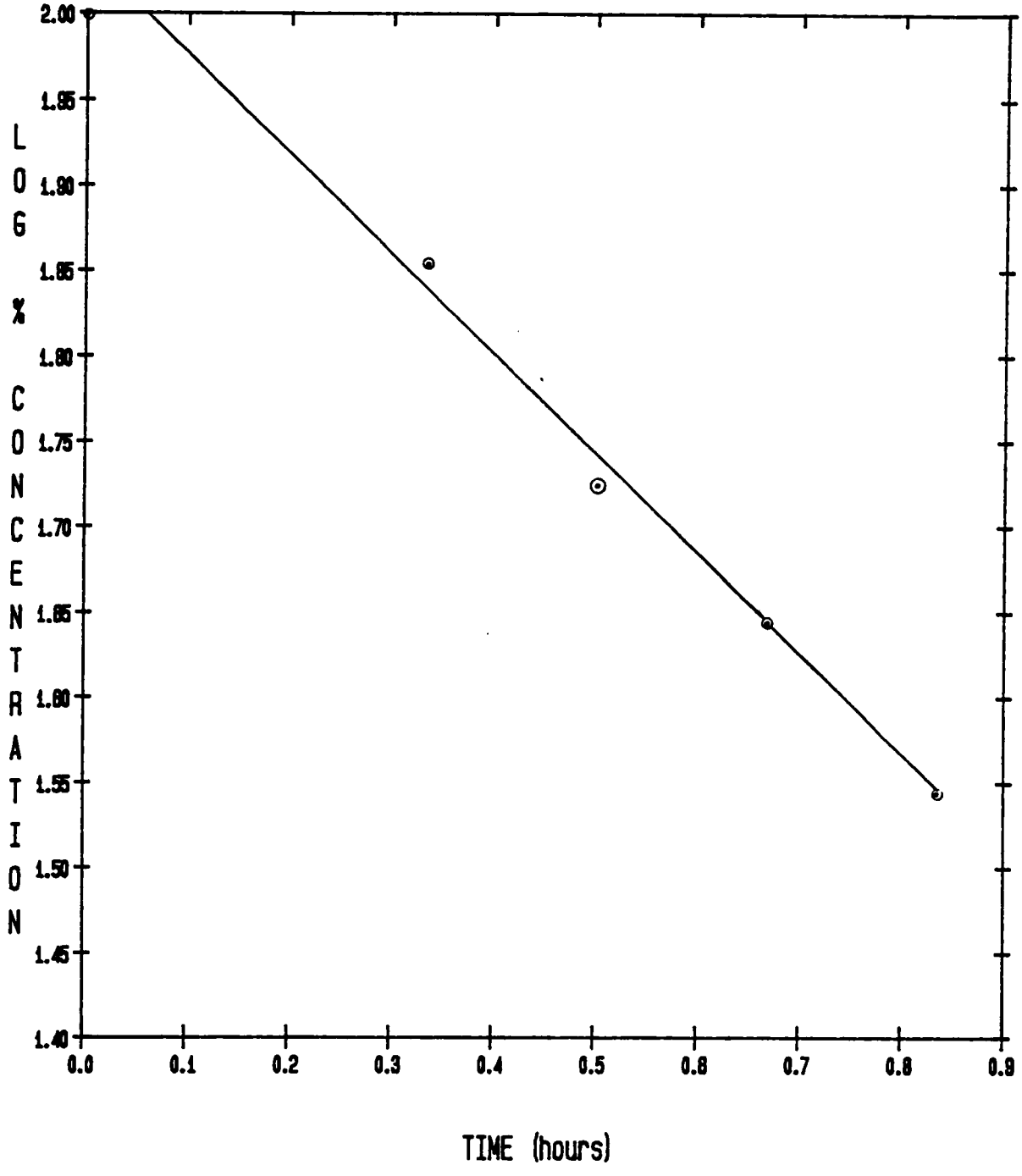


Fig. 17. Variation with time of the logarithm of the concentration of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 200 ± 0.8°C

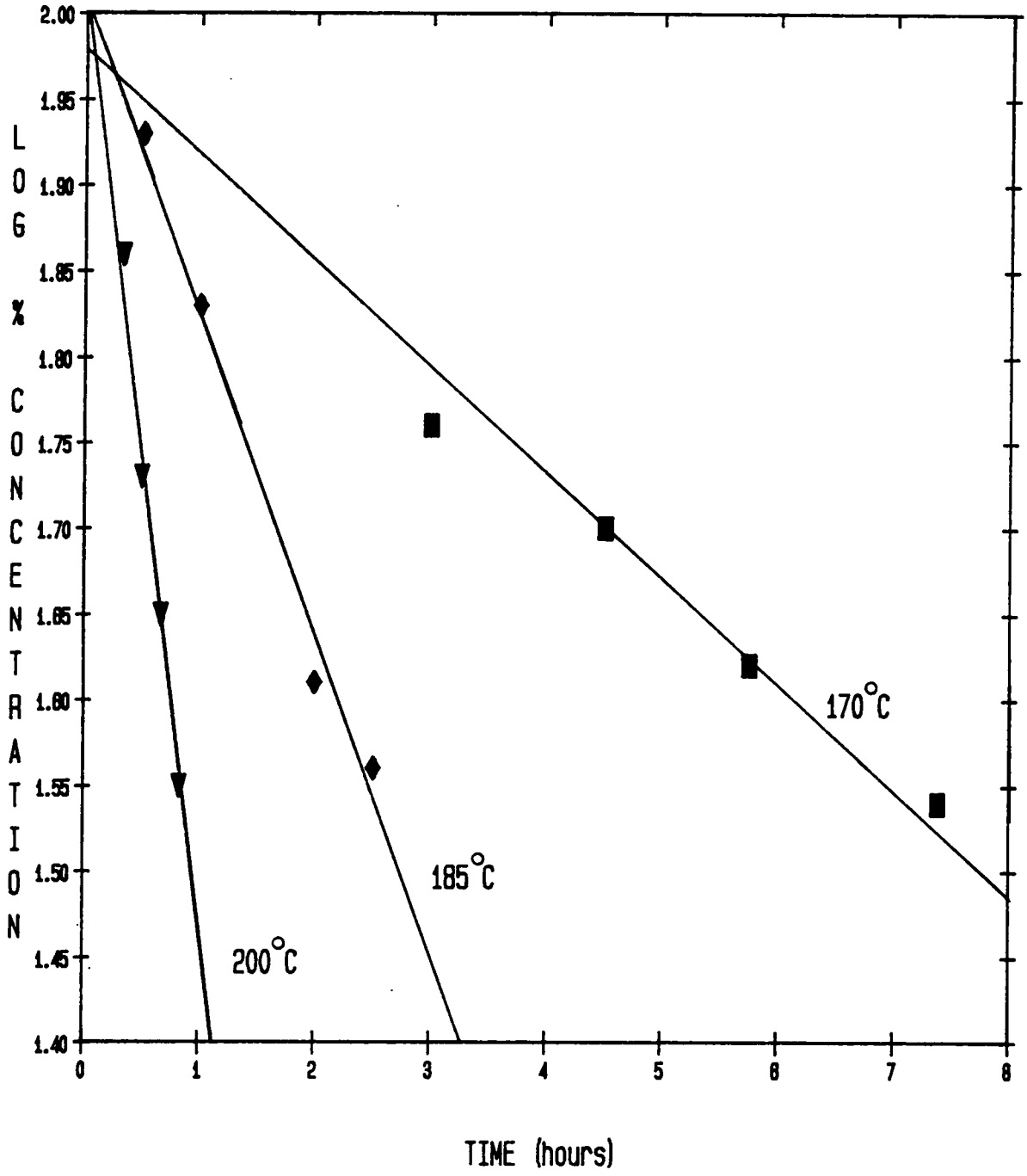


Fig. 18. Variation with time of the logarithm of the concentration of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol over the temperature range of 170-200°C

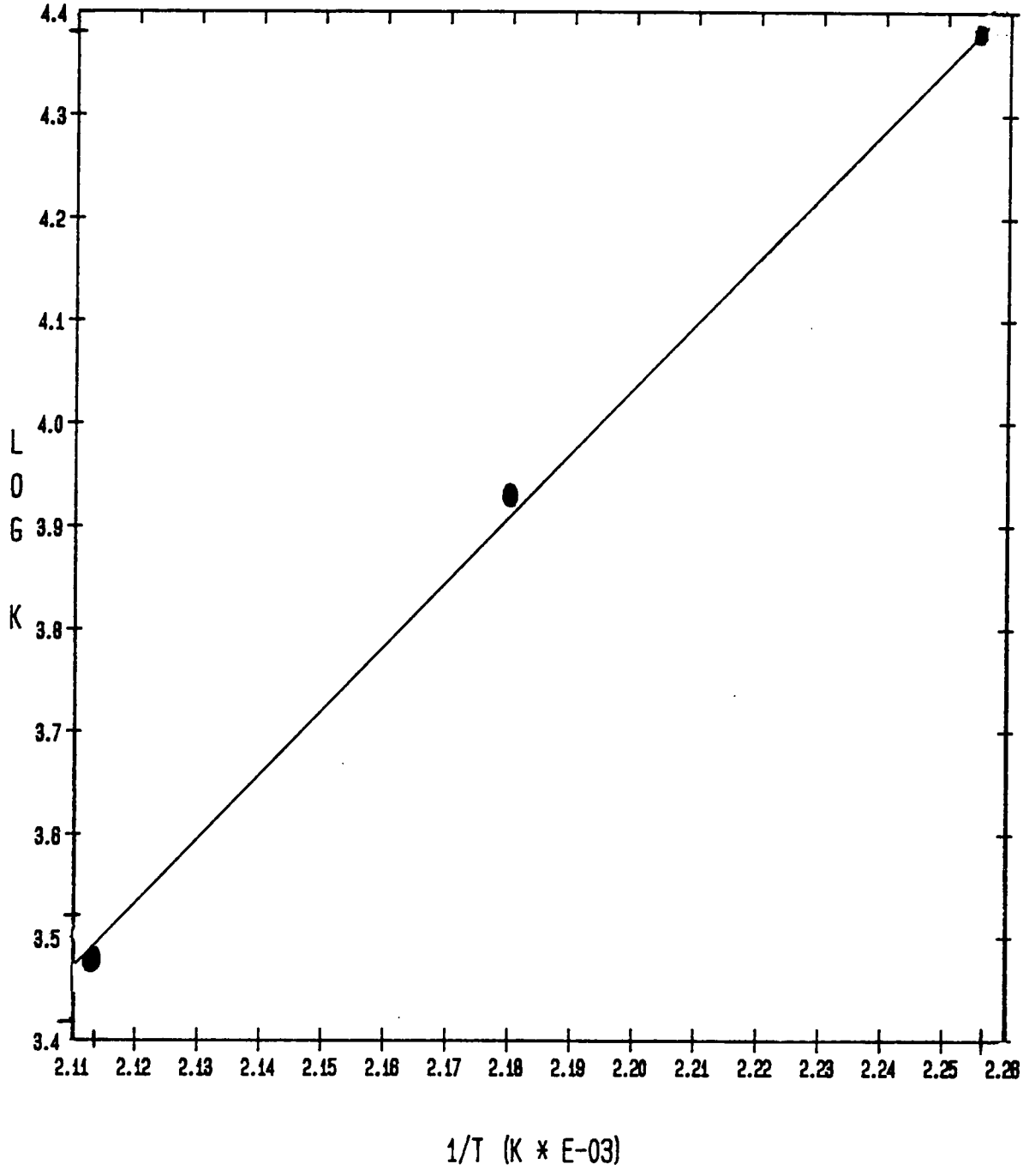


Fig. 19. Variation of Log k versus 1/T over the temperature range of 170-200 ± 0.6°C for the evaluation of E_a of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

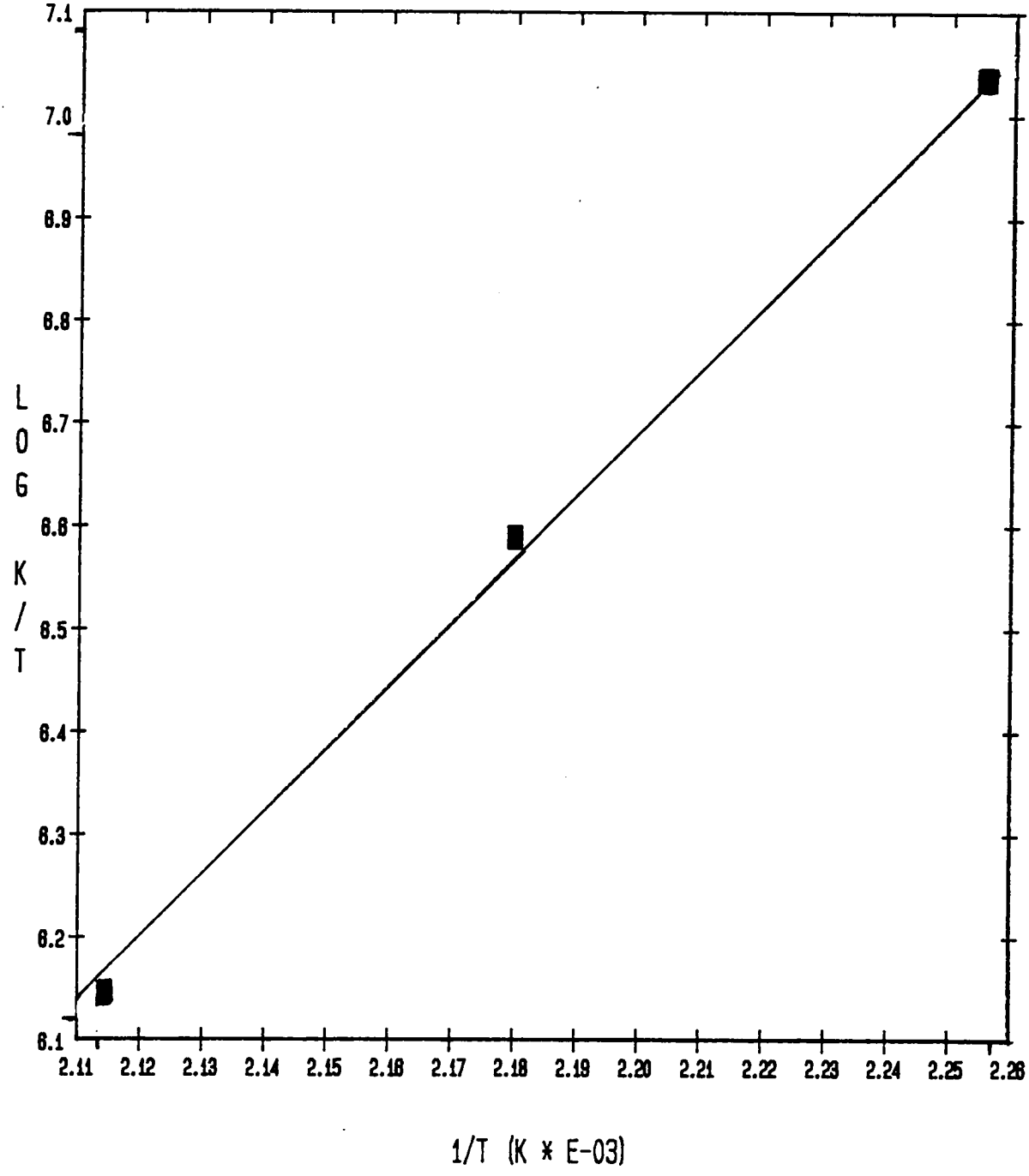


Fig. 20. Variation of Log (k/T) versus 1/T over the temperature range of 170-200 ± 0.6°C for the evaluation of ΔH of 2,5-diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

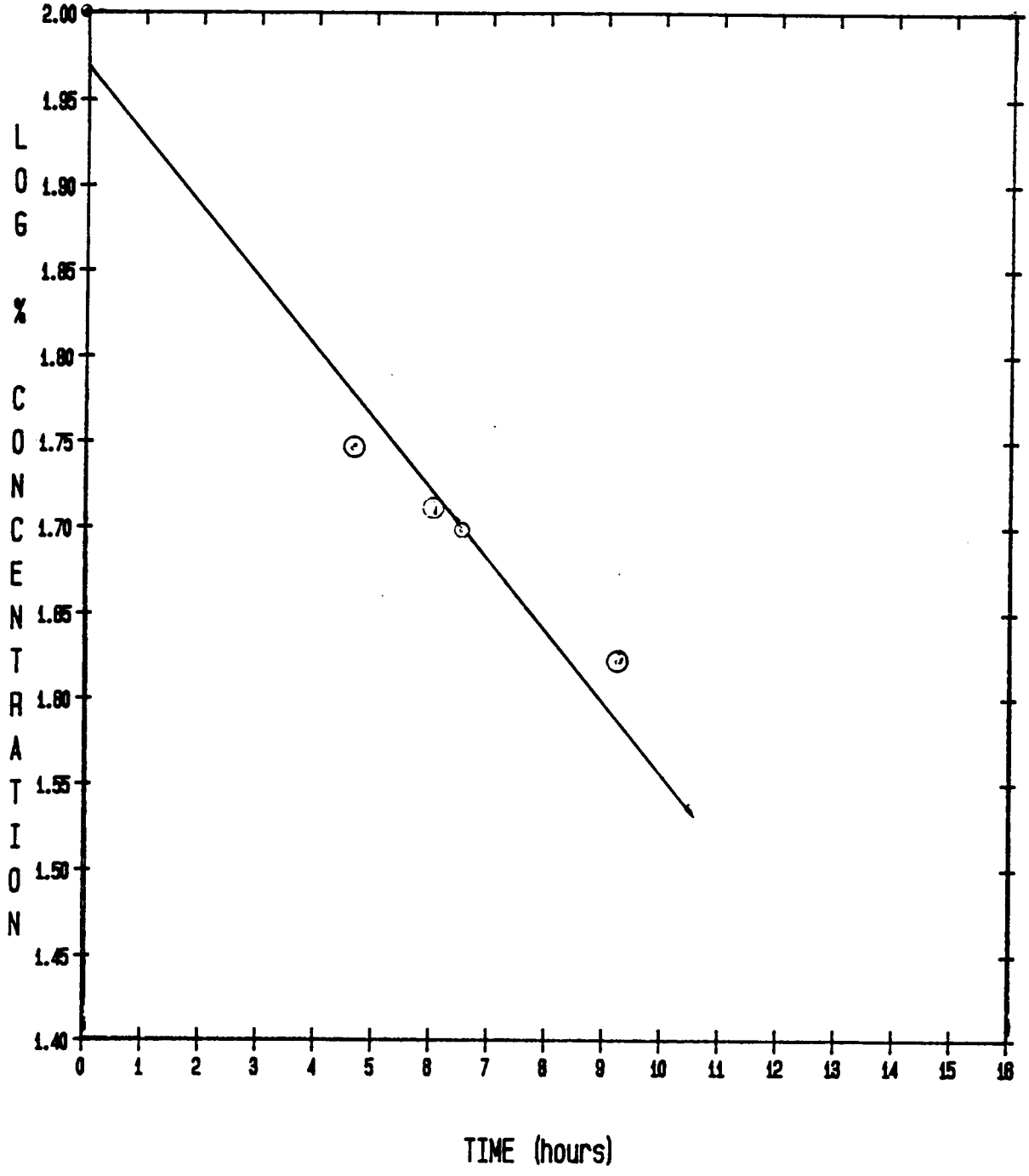


Fig. 21. Variation with time of the logarithm of the concentration of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 170 ± 0.6°C

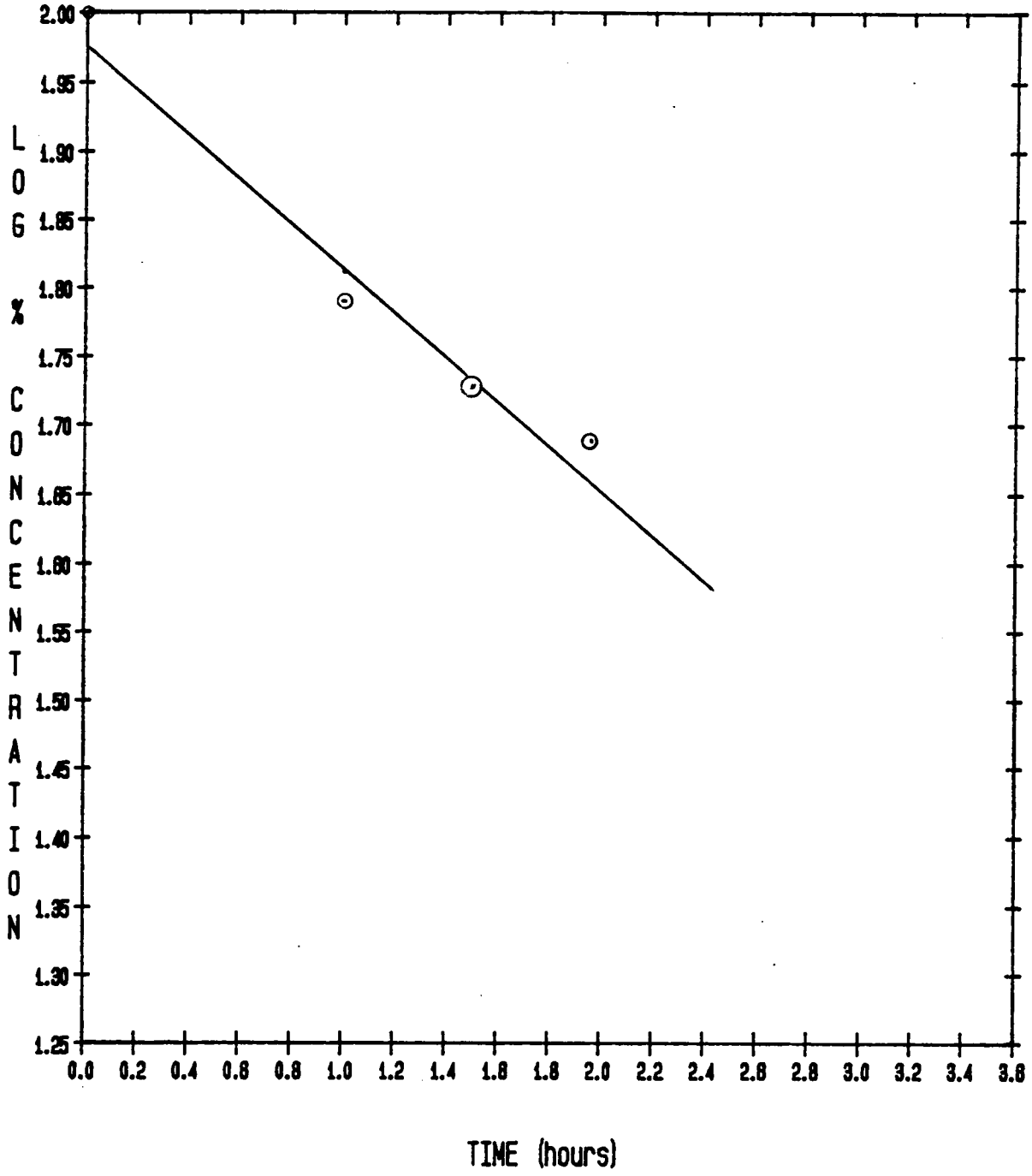


Fig. 22. Variation with time of the logarithm of the concentration of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 185 ± 0.8°C

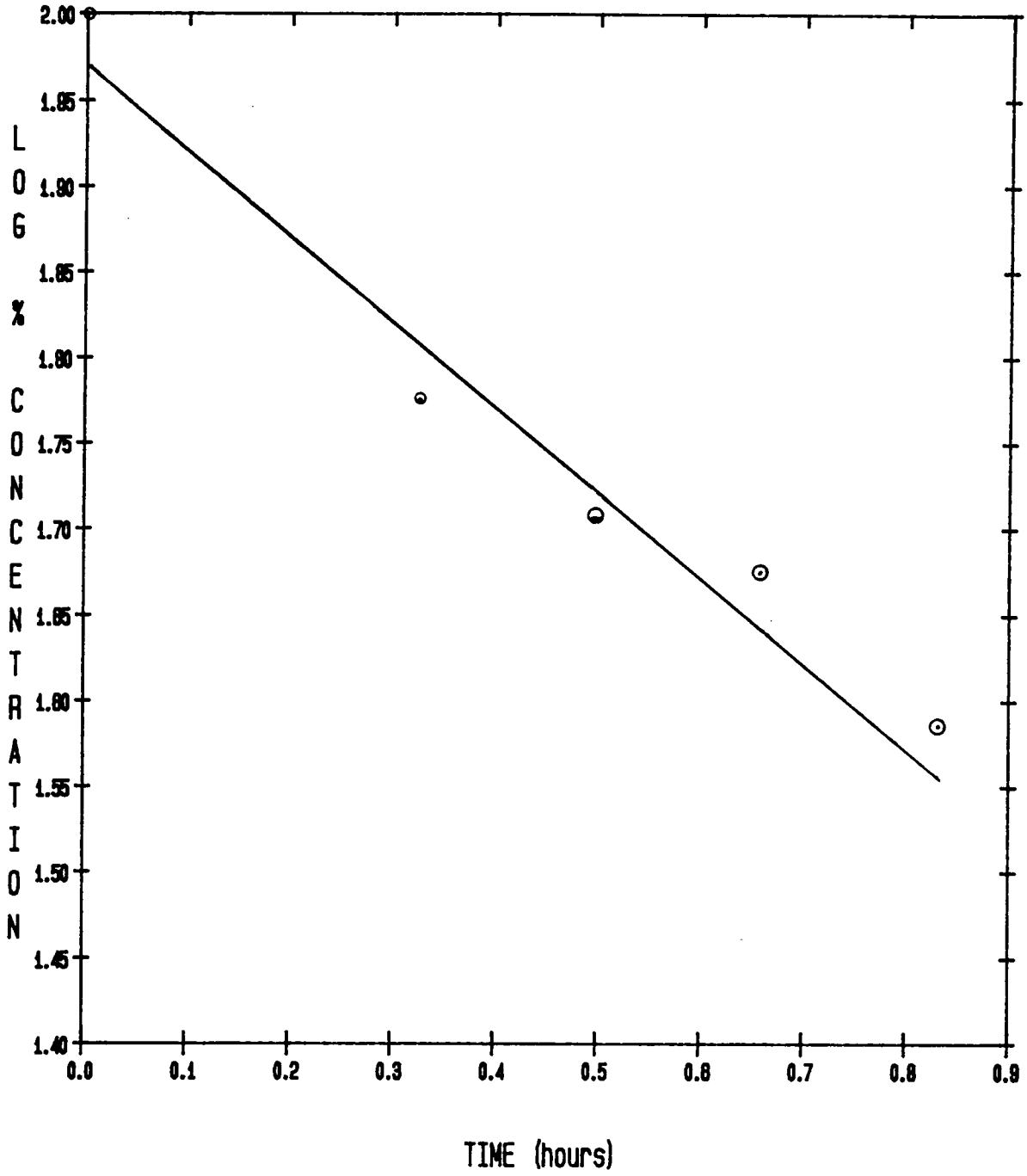


Fig. 23. Variation with time of the logarithm of the concentration of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 200 ± 0.8°C

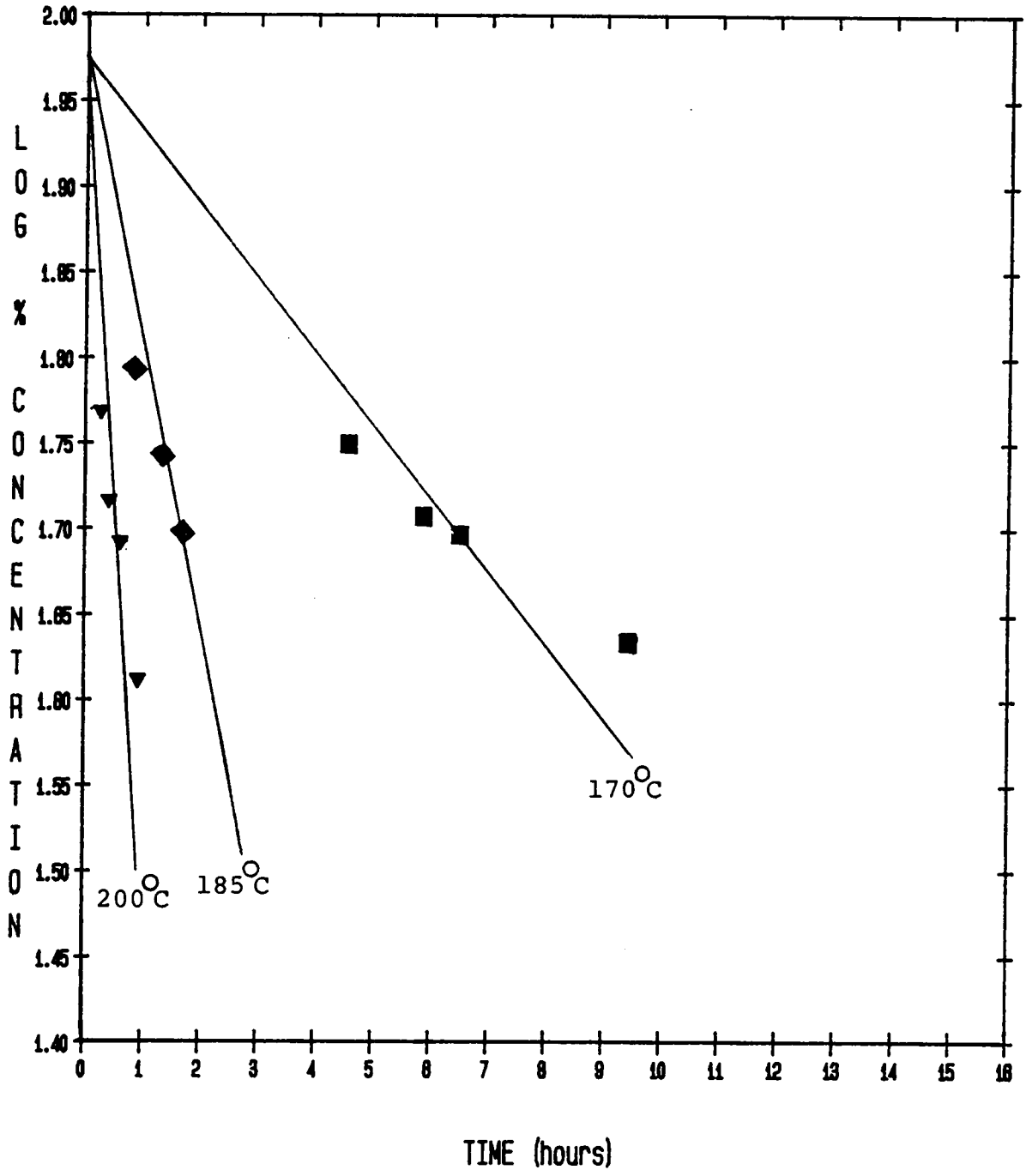


Fig. 24. Variation with time of the logarithm of the concentration of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 170-200° C

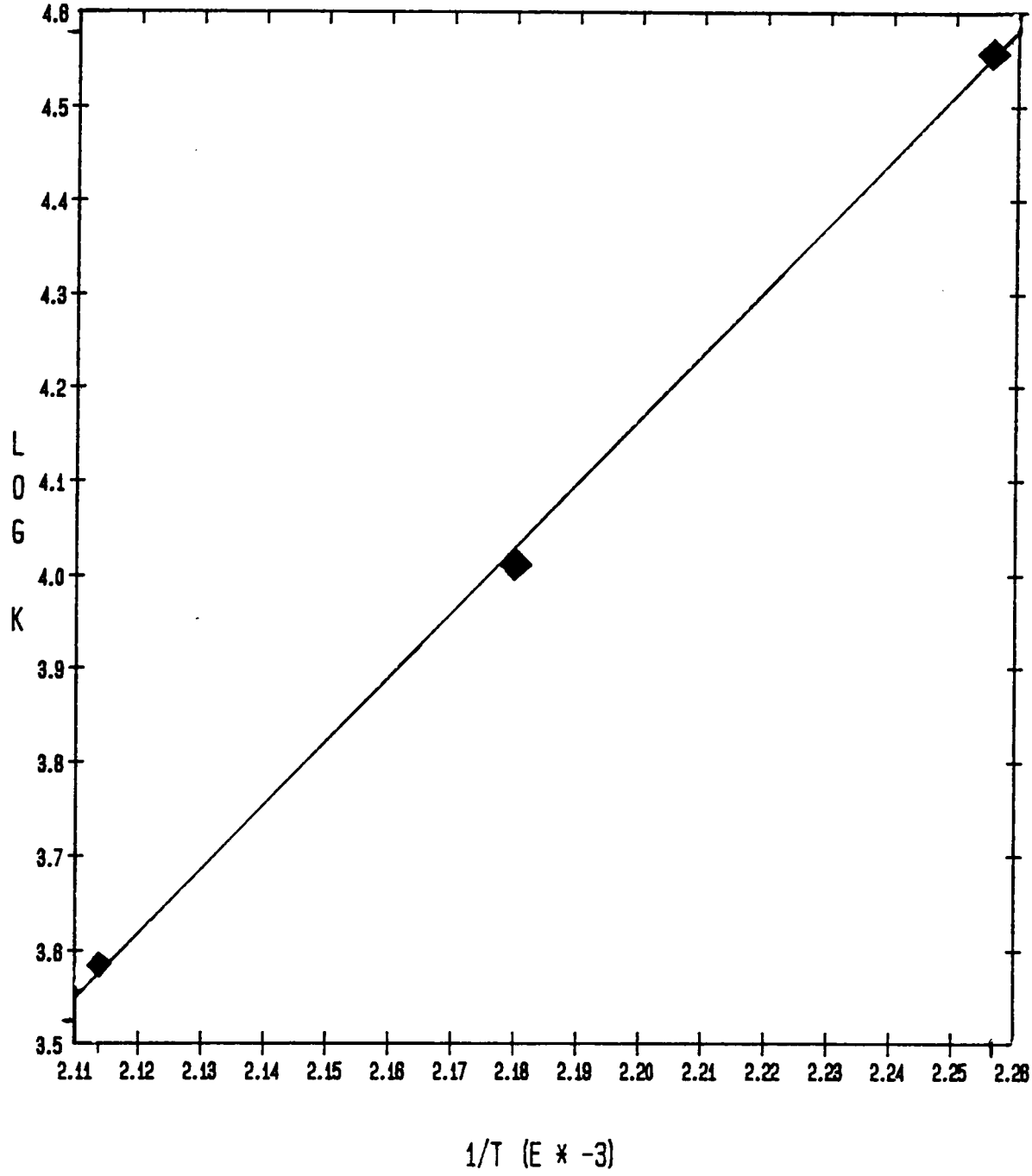


Fig. 25. Variation of Log k versus 1/T over the temperature range of 170-200 ± 0.5°C for the evaluation of E_a of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

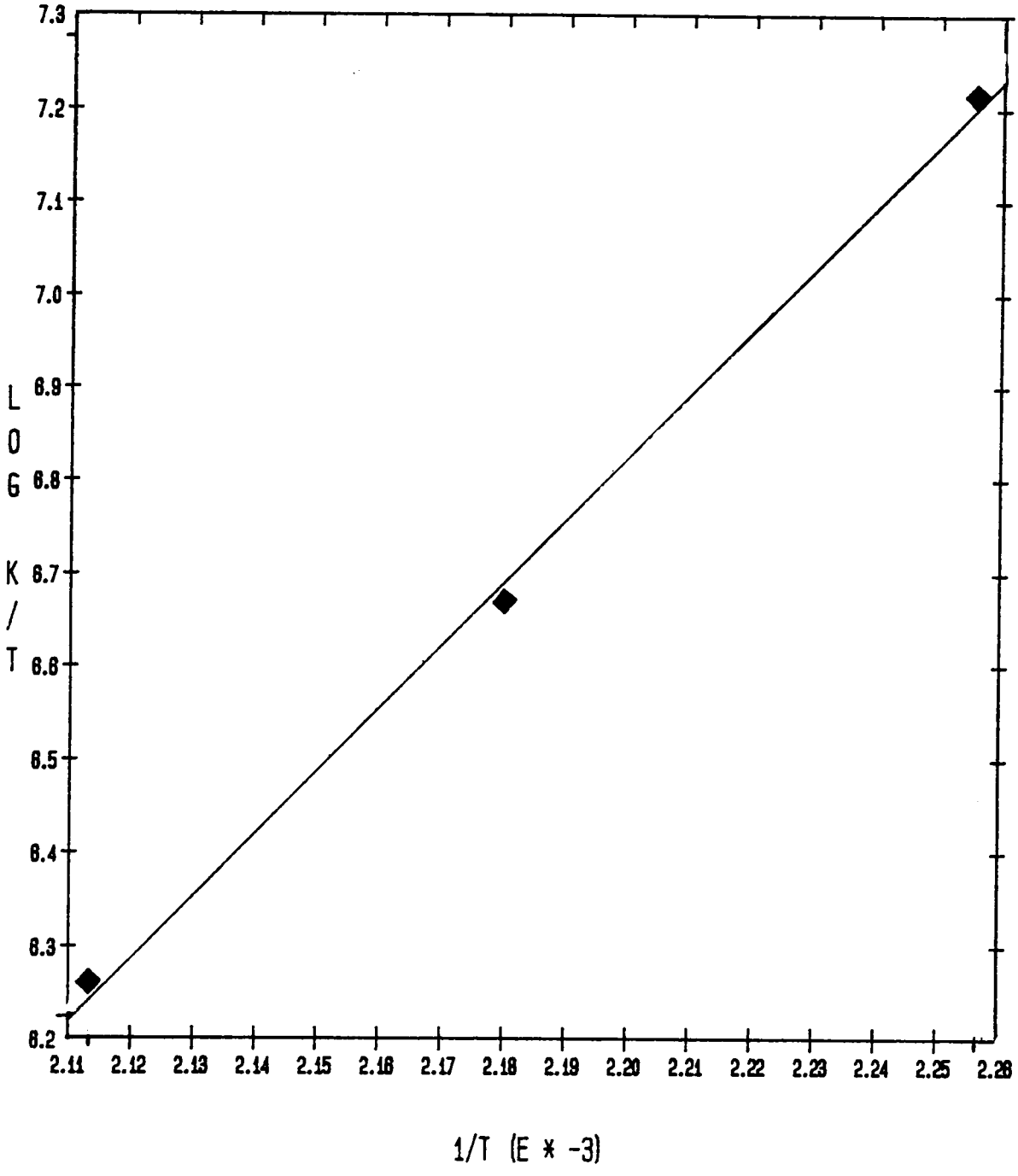


Fig. 26. Variation of Log (k/T) versus 1/T over the temperature range of 170-200° C for the evaluation of ΔH of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

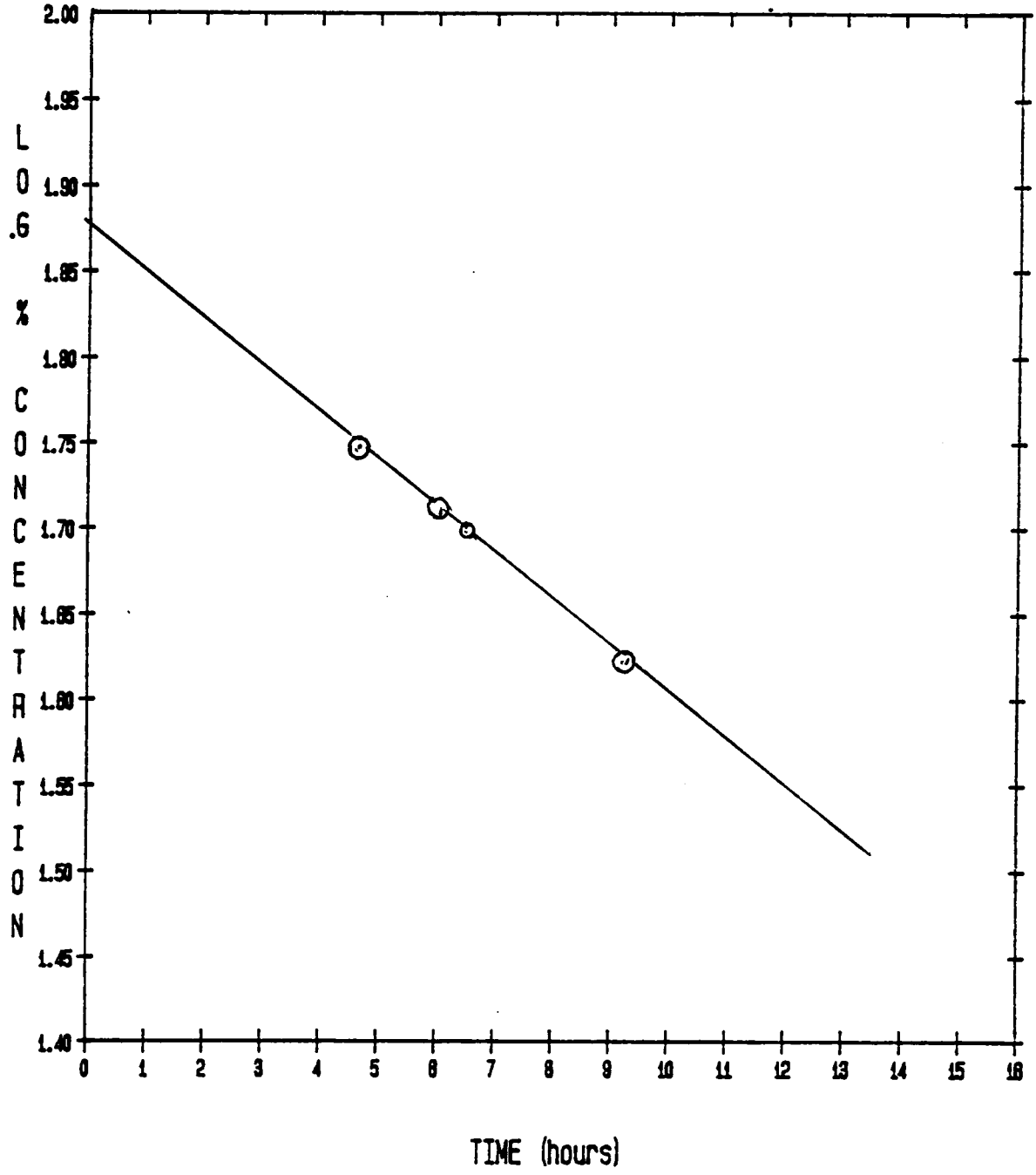


Fig. 27. Variation with time of the logarithm of the concentration of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 170 ± 0.6°C eliminating the zero point

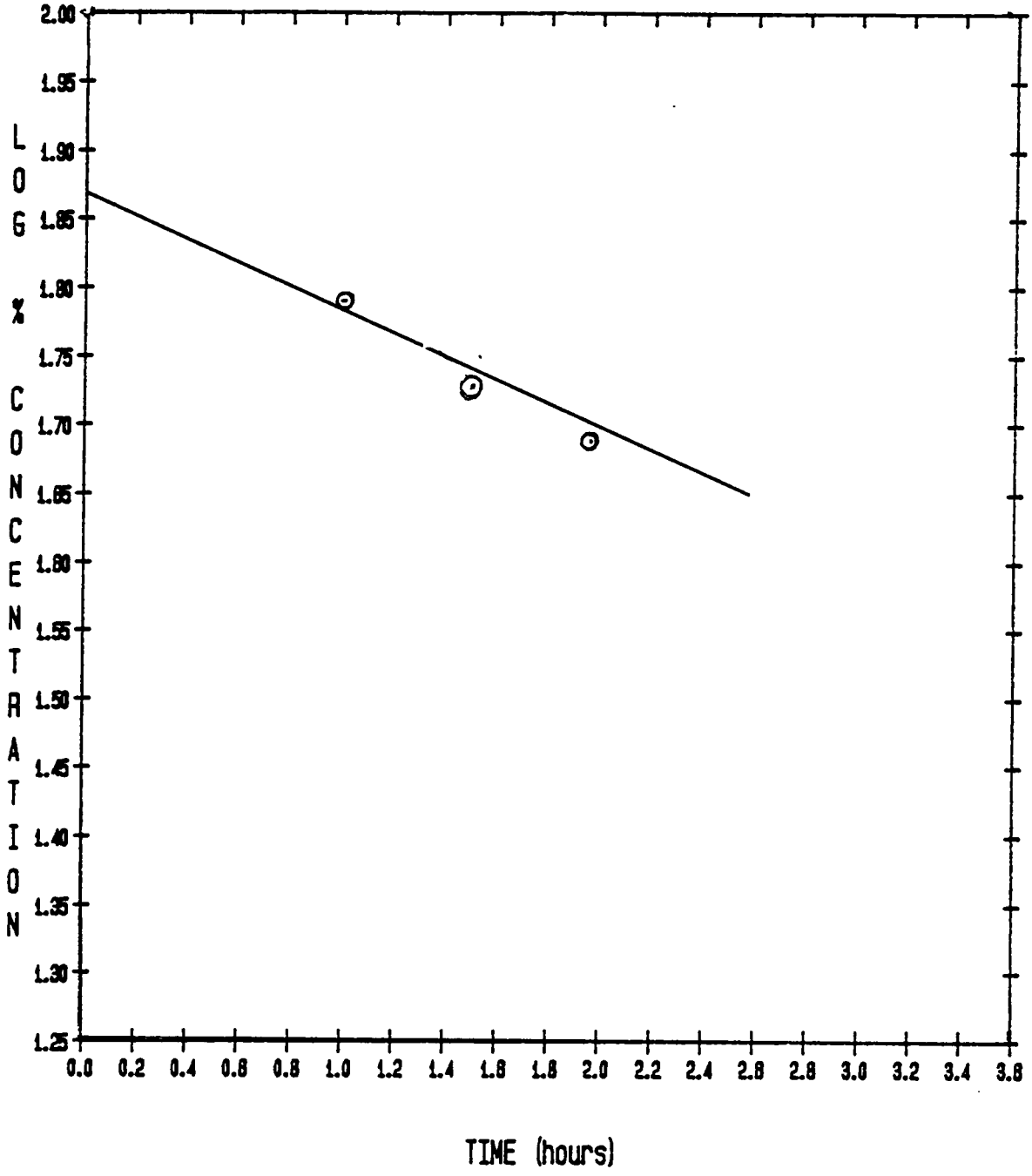


Fig. 28. Variation with time of the logarithm of the concentration of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 185 $\pm$ 0.8°C eliminating the zero point

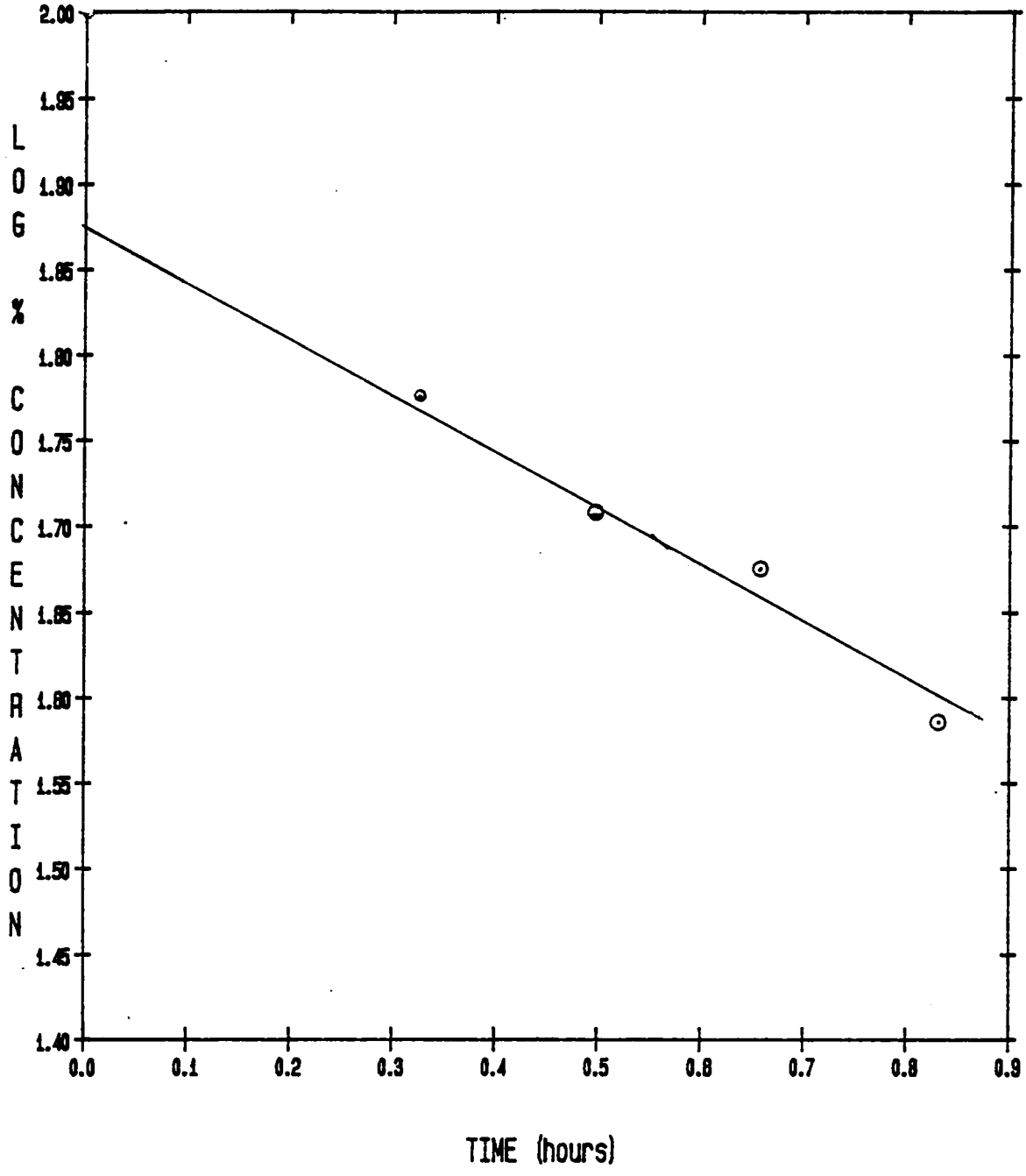


Fig. 29. Variation with time of the logarithm of the concentration of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 200 $\pm$ 0.8°C eliminating the zero point

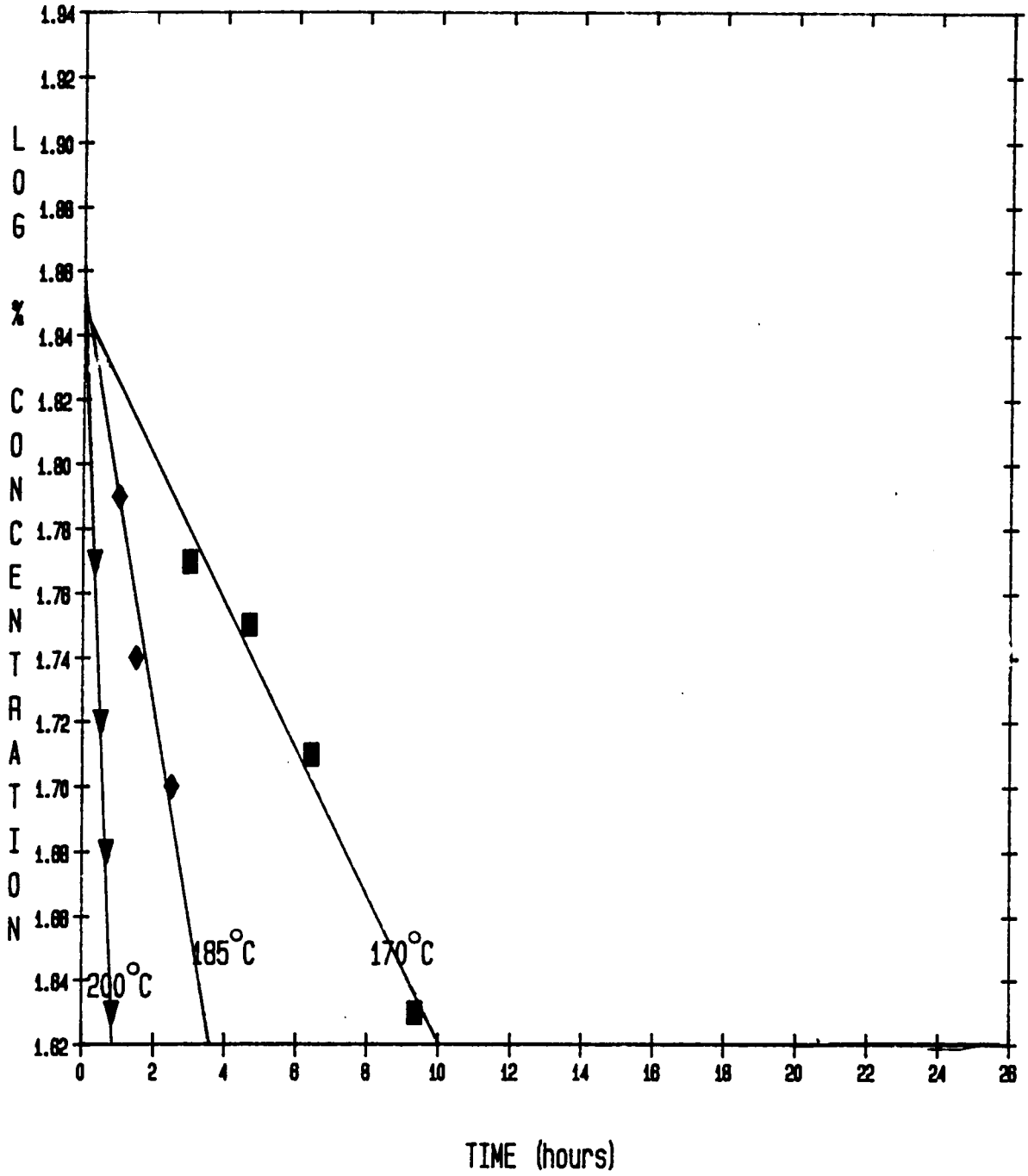


Fig. 30. Variation with time of the logarithm of the concentration of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol at 170-200°C eliminating the zero point

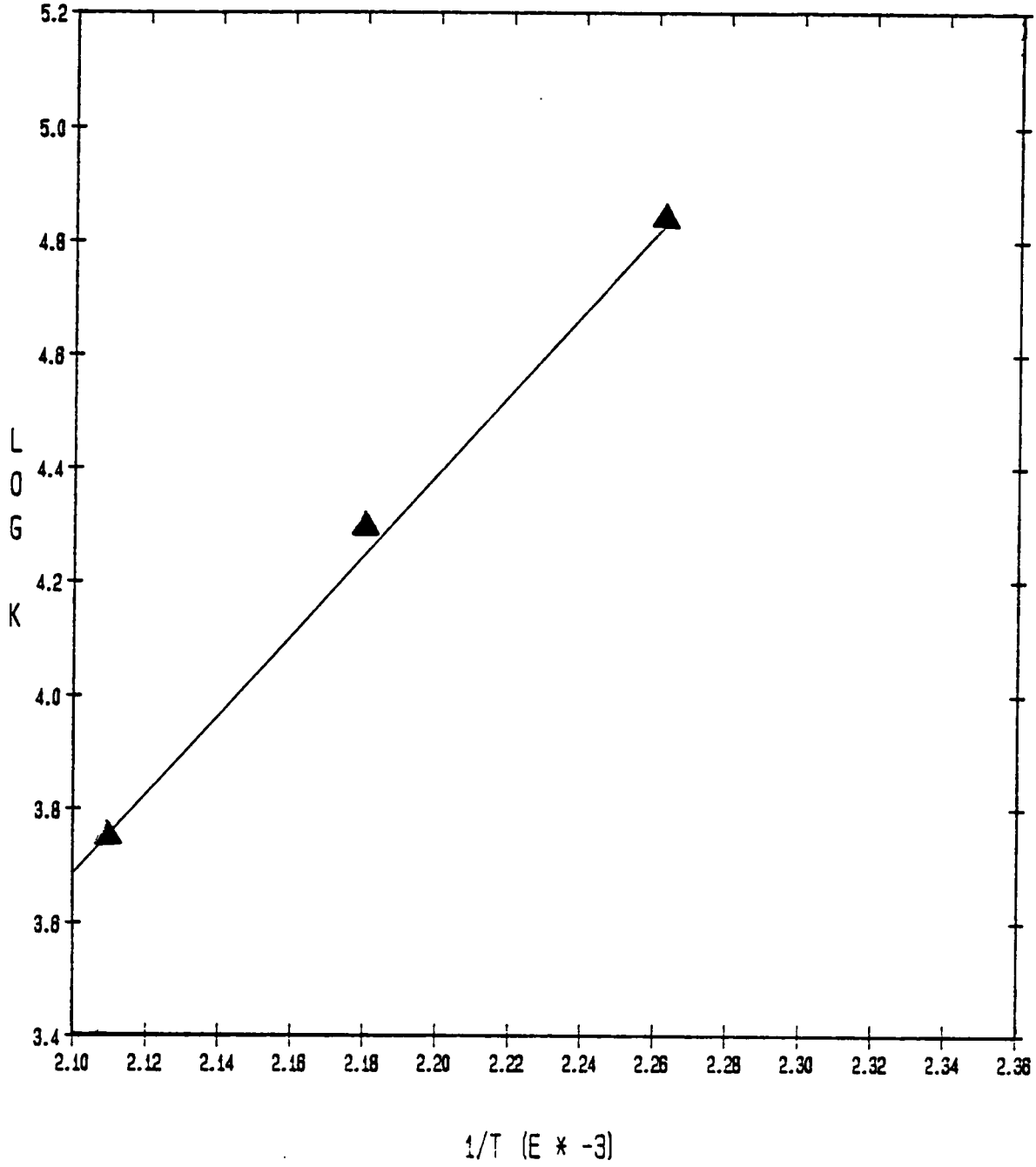


Fig. 31. Variation of Log k versus 1/T over the temperature range of 170-200 ± 0.5°C for the modified evaluation of E_a of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

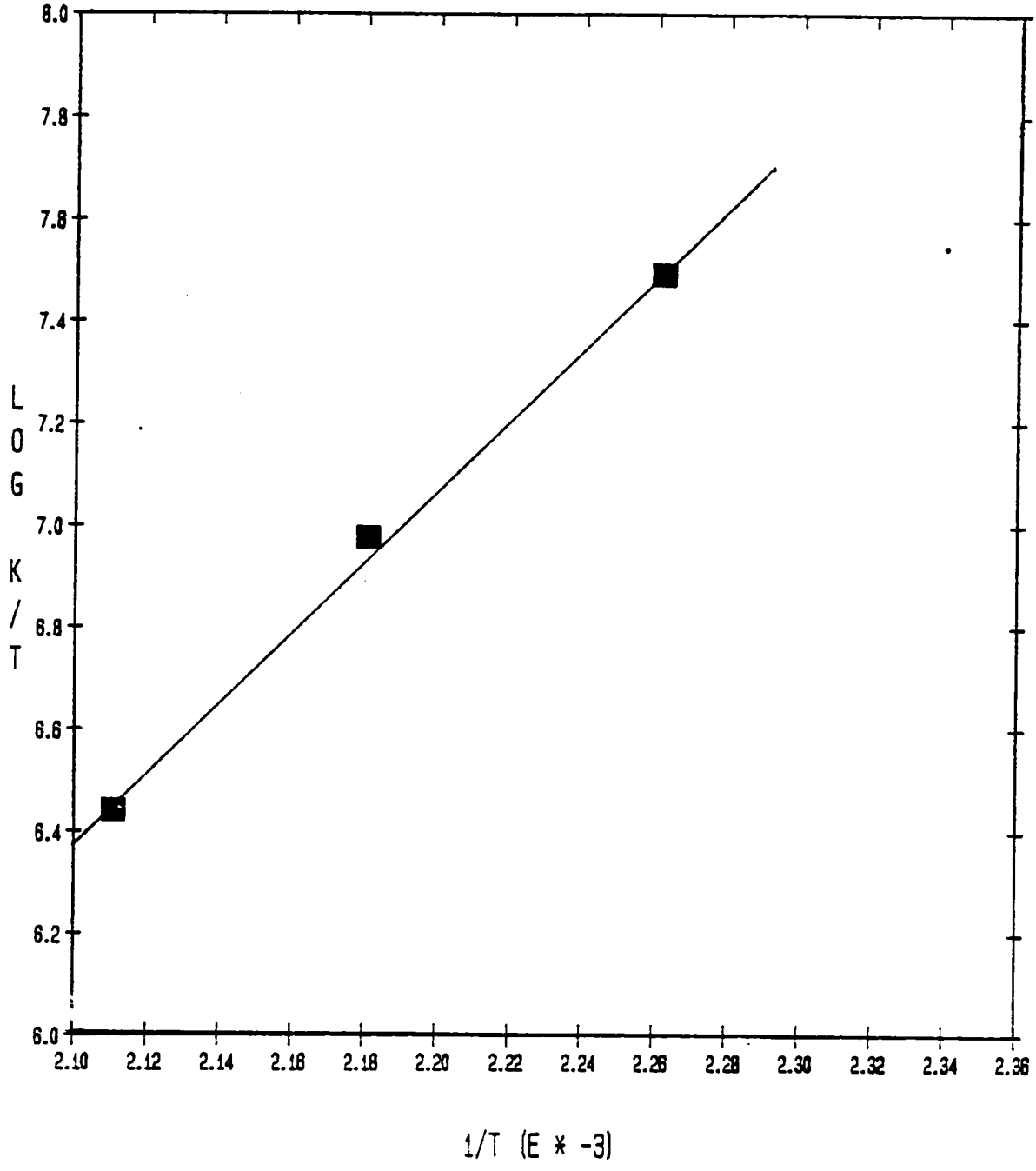


Fig. 32. Variation of Log (k/T) versus 1/T over the temperature range of 170-200°C for the modified evaluation of ΔH of 2,5-dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

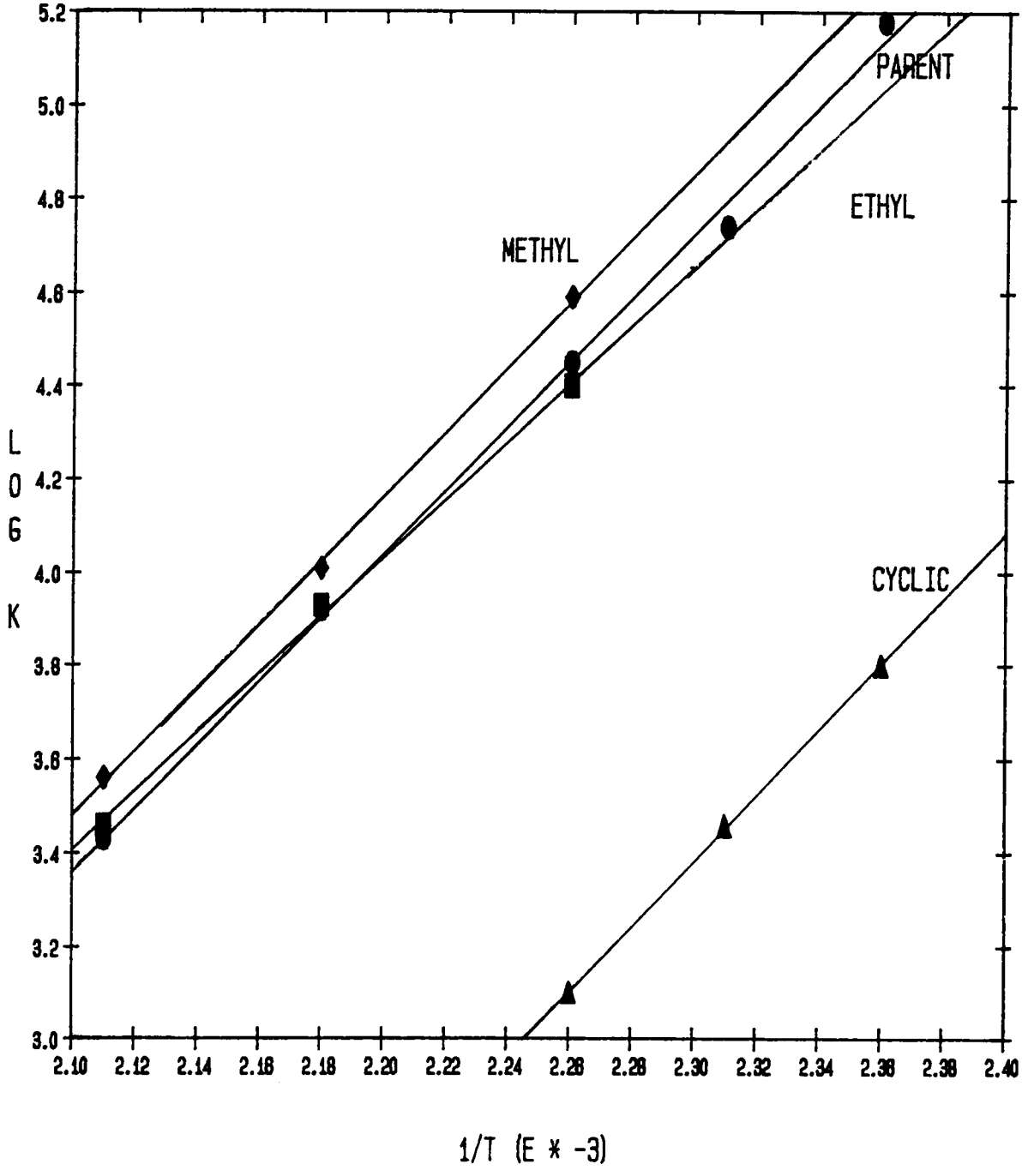


Fig. 33. Variation of Log k versus 1/T over the temperature ranges for the evaluation of Ea for all alcohols

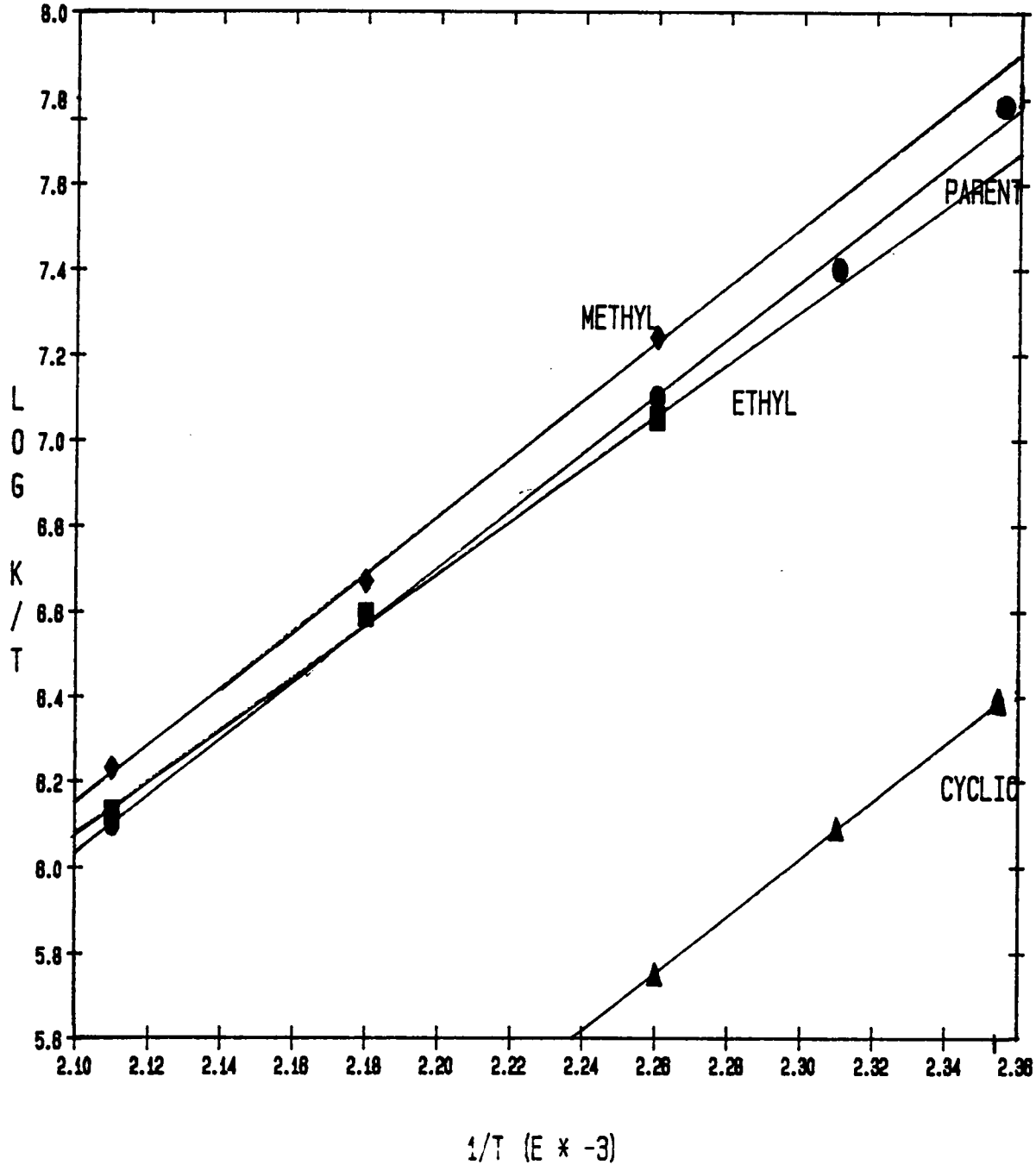


Fig. 34. Variation of Log (k/T) versus 1/T over the temperature ranges for the evaluation of ΔH for all alcohols

V. Discussion

A. Synthesis of 2,5-Dialkyl-3,4-diphenyl-2,4-cyclopentadien-1-ones.

The synthesis of these compounds with the exception of 2,5-di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (16), was accomplished by base catalyzed condensation of benzil with the appropriate ketone to form an intermediate alcohol which could be dehydrated to form the desired compound. The success at synthesizing the compounds where the alkyl groups were ethyl, methyl, and cyclic dodecane and the lack of success at synthesizing the compounds where the alkyl groups were isopropyl or larger, even under forced conditions, indicated that there is an energy barrier or steric constraint that prevents the condensation from occurring.

If the results of the condensation of the successful cases are reviewed, it is clear that the condensation is greatly favored. In the case where the alkyl group was methyl, the yield obtained for the intermediate alcohol was 95% and that for the case where the alkyl groups were ethyl was 98%. Clearly, the high yields reflect a low steric hindrance to the reaction. If the result for the case where the alkyl group was cyclic dodecane are considered, it is seen that this intermediate alcohol was formed in 87% yield. This decrease, although small, may be due to strain caused by the cyclic ketones interaction with the benzil during

condensation. Others have investigated this type of condensation and found that the cyclic ketones must be large enough to allow interaction with benzil or there will be no condensation.[14]

Allen and Van Allen [12] reported that 2,6-dimethyl-4-heptanone did not condense with benzil even under forced conditions. The results of this work lend support to that statement. It appears that the extra methyl group of 2,6-dimethyl-4-heptanone interacts enough with the benzil to keep the intermediate anion from reacting regardless of the base used. If, however, an electrophile less hindered than benzil was used, such as benzaldehyde, the decreased size of the electrophile permits proper interaction between the nucleophile and electrophile and thus proper reaction.

It is apparent from this work that weaker bases are better than stronger bases in these condensations. The results indicate that the use of strong bases lowers the yield of model compounds and leads to undesired side reactions.

Once the intermediate alcohols were formed, they were dehydrated under mild conditions to give the needed dienones. The ease of the dehydration and the high yields obtained for all alcohol dehydrations are probably due to the increased stability that the dienone systems have compared to the intermediate alcohols. This is even more readily seen in fully aromatic tetracyclone which forms the

dienone system without normally stopping at the intermediate alcohol stage. Here, the driving force was not only to form the dienone system but also to form a system that is conjugated to the aromatic rings.

B. Synthesis of Alcohols

1. Choice of Reagent

The alcohols that were needed for the kinetic studies were synthesized using both phenyllithium and Grignard reagents in order to establish which reagent would be better for reaction with these ketones. The following table summarizes the data for the organometallic reactions.

Table II

Results For The Reactions Of Precursor Ketones With The Organometallic Reagents

Alcohol	% Yield PhMgBr	% Yield PhLi	mp
Parent	68.5	86.5	176-178
Ethyl	66.0	77.7	oil
Cyclic	32.2	66.3	128-129.5
Methyl	33.0	2.7	137-138
t-Butyl	-	89.0	oil

In general, it was found that depending upon the ketone both phenyllithium and the Grignard reagent were useful for

the synthesis of these alcohols. However, phenyllithium is the reagent of choice because: 1) The formation of this reagent was quicker and more quantitative than for the Grignard reagent, 2) The yields and purity of the products obtained from the reactions of phenyllithium with these ketones were better than those for similar reactions using the Grignard reagent, and 3) the phenyllithium reactions could be performed at a lower temperature than the Grignard reactions, thus eliminating the chance of rearrangement of the initially formed anion.

These results may be due to the fact that lithium metal is more reactive than magnesium, and thus it forms the reagent under milder conditions and in better yields. Also, the organometallic bond of the phenyllithium causes the phenyllithium to be a more reactive species than its organomagnesium counterpart. This increases the yields, purity, and rate of reaction of the phenyllithium reaction relative to the Grignard reagent.

2. Reactions of The Ketones With Organometallic Reagents

With the exception of 2,5-dimethyl-3,4-diphenyl-2,4-cyclopentadien-1-one-dimer (dimethyl cyclone, 14) whose reaction will be discussed later, these ketones were more reactive than tetracyclone itself. It was found that less reagent and milder conditions were needed for these ketones than was needed for tetracyclone. In general these ketones

reacted at temperatures that were 8 to 10 degrees lower than for similar reactions of tetracyclone with phenyllithium.

The following observations can be made about the ketone individually.

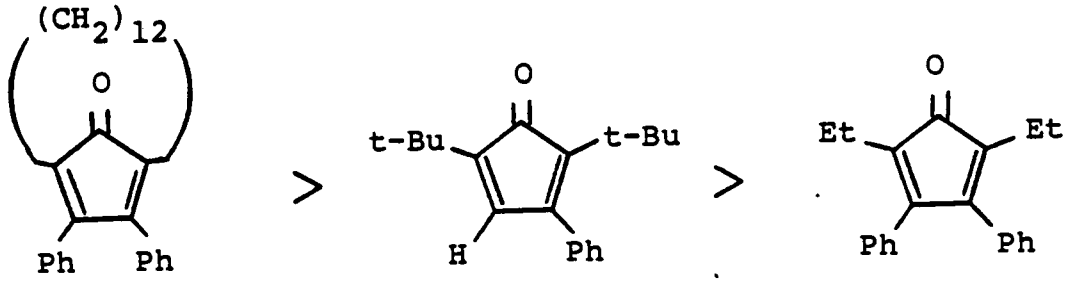
In the case of the dimethyl cyclone, the reaction with the organometallic reagents was slower and less efficient because the dimethyl cyclone, had to dissociate before the alcohol could form. Since the dimethylcyclone was only 20% dissociated in boiling benzene,[8] the reaction must be forced to obtain only small yields. The purification of this alcohol was difficult because the final product is a mixture of the desired alcohol, dimer, and partially reacted dimer.

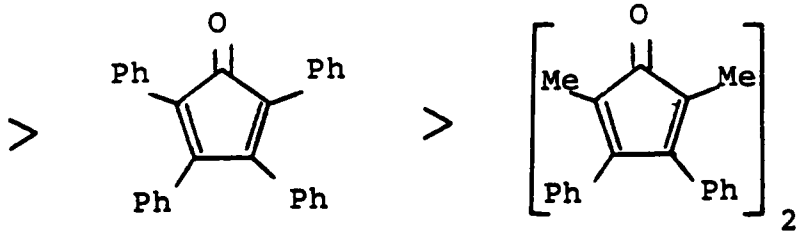
The reaction of 2,5-diethyl-3,4-diphenyl-2,4-cyclopentadiene-1-one (diethyl cyclone, 15) with the organometallic reagents more closely resembled the parent ketone than did the other ketones. The reaction could be performed using the Grignard reagent at elevated temperatures without rearrangement of the initially formed anion. It was found that the diethyl cyclone could also be reacted with either phenyllithium or Grignard reagent at ice bath temperatures to give the same product as in the high temperature reaction. The major drawback to these reactions was that the product was an oil which did not crystallize, making purification difficult.

The reaction of 15,16-diphenylbicylclo[12.2.1] heptadeca-14,16-dien-17-one (cyclic cyclone, 17) was faster than any other ketone studied using either phenyllithium or phenylmagnesium bromide as reagent. The reason for this may be that the second ring of the cyclic cyclone causes the carbonyl to be strained. Reaction of the carbonyl to form an alcohol relieves this strain by changing the bond angles. Because this strain may also affect the rearrangement of the initially formed anion of the cyclic alcohol, it is extremely important that this reaction be run and quenched at very low temperatures (0 to -10°C).

The results obtained from the reaction of 2,5-di(t-butyl)-3-phenyl-2,4-cyclopentadien-1-one (di(t-butyl) cyclone, 15) with phenyllithium were surprising. It was expected that the reaction of the carbonyl function of the di(t-butyl) cyclone with phenyllithium would be hindered by the presence of the two t-butyl groups which were adjacent to it. The opposite proved to be true. The di(t-butyl) cyclone reacted almost as fast as the cyclic cyclone. The reason for this is not known but it is clear that the two t-butyl groups do not sterically hinder the reaction. There may also be strain in this case that is caused by one of the t-butyl group's interactions with the phenyl ring. Formation of the alcohol may relieve some of this strain by allowing the t-butyl group to be in a conformation that does not interact with a phenyl ring.

The order of reactivity of these ketones with organometallic reagent are as follows





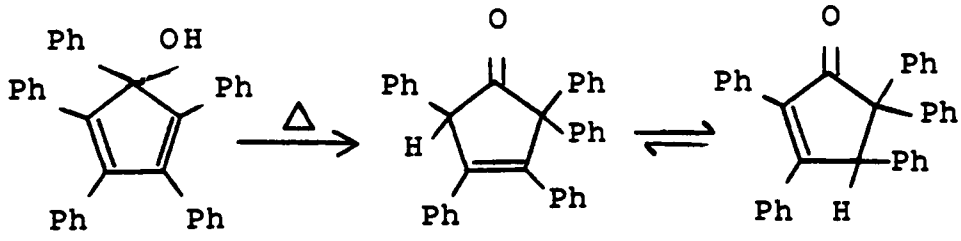
C. Rearrangement of the Dialkyl Alcohols

All of the alcohols were rearranged thermally to isolate the products from the reaction and to determine the rate of the reaction.

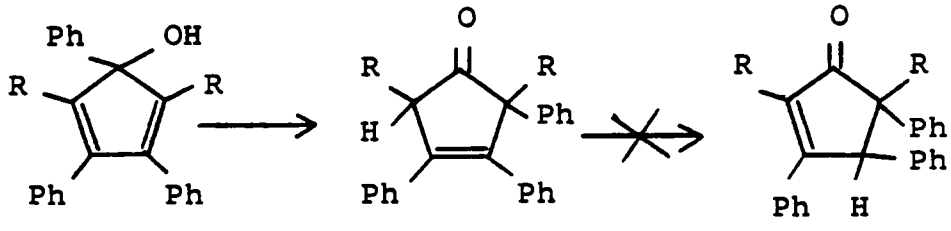
1. Rearranged Dialkyl Ketones

The cases where the 2 and 5 position of the cyclopentadien-1-ols are occupied by alkyl groups give different products than those obtained for the fully aromatic system. When the dialkyl alcohols bearing methyl, ethyl, and cyclic dodecane substituents at the 2 and 5 position were rearranged, only the unconjugated isomer was obtained; whereas,

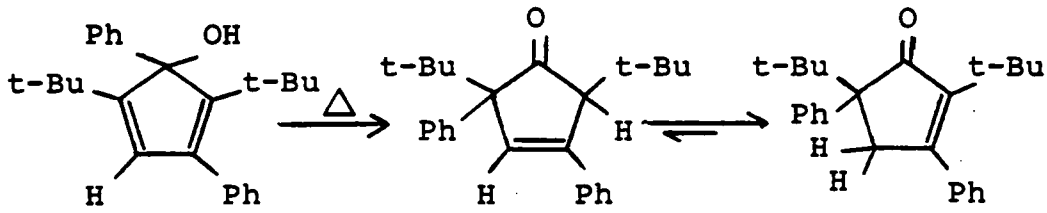
rearrangement of the fully aromatic system gives both possible isomers. The reason for this may be that when the fully aromatic system rearranges, the kinetic product is the unconjugated ketone. Under the conditions of the reaction, the thermodynamic product, the conjugated ketone, begins to slowly form as is indicated below:



When the dialkyl alcohols were rearranged the kinetic product was also formed initially. Since the conjugated ketone is no more stable than the unconjugated ketone, there is no driving force for the isomerization to occur.



The rearrangement of the di(t-butyl) alcohol did display different behavior than the other dialkyl alcohols. When the products of this rearrangement were analyzed after 196 hours, there was a mixture of both conjugated and unconjugated ketones. The reason for this may be that in this case, the thermodynamic product is more stable than the kinetic product. By examining the structures of the ketones in question it is clear that the conjugated ketone is more stable because the double bond is of greater substitution.



Another way that the dialkyl ketones differ from the parent ketone is stereochemical. In the parent ketone, stereoisomers are easily observed in both ^{1}H and C_{13} NMR spectrum of these compounds. For the rearranged dialkyl ketones the presence of stereoisomers is not readily discerned and may in fact suggest that there is only one isomer present in the purified compound. This effect is seen in both ^{1}H and C_{13} NMR spectrum of these molecules. The reason for this may either be that the amount of one stereoisomer

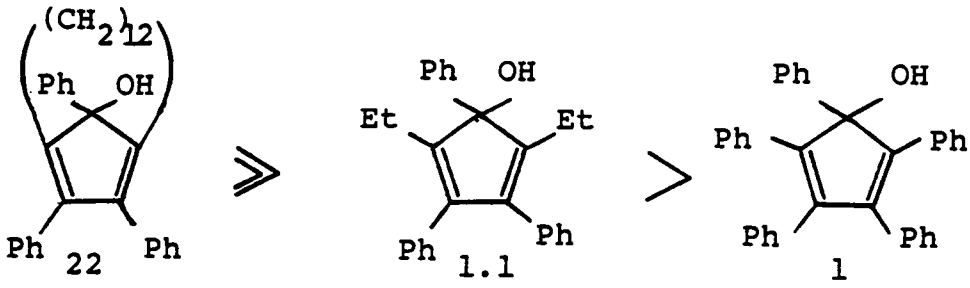
is so small as to not be seen, or that one stereoisomer has been removed during repetitive recrystallization. The latter explanation appears to be the more plausible since it is unlikely that only one stereoisomer is formed in this reaction.

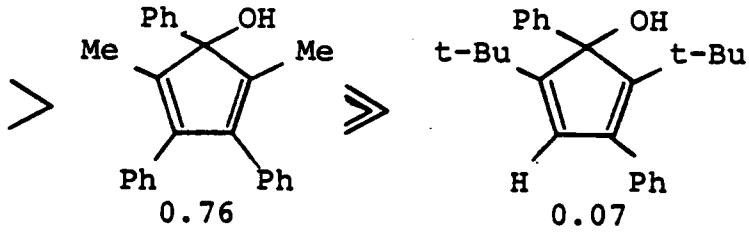
2. Kinetics of the Rearrangement

All of the alcohols were rearranged to establish the relative rates for the rearrangement. All alcohols, except for the di(t-butyl) alcohol, were studied to obtain kinetic information. The di(t-butyl) alcohol was studied only as an extension of the current problem and only to establish its rate relative to the parent alcohol. This compound lacks a phenyl ring on the 4-position of the cyclopentadien-one ring and is different enough from the others as to make comparison of data meaningless. By doing a relative rate study, it could be shown whether or not the alcohol could be rearranged and how it compared to the other alcohols. However, the results could not be interpreted as being due to the t-butyl groups or to the missing phenyl ring.

a. Relative Rates

The relative rates for the rearrangement of all alcohols were obtained and are illustrated by the following scheme.

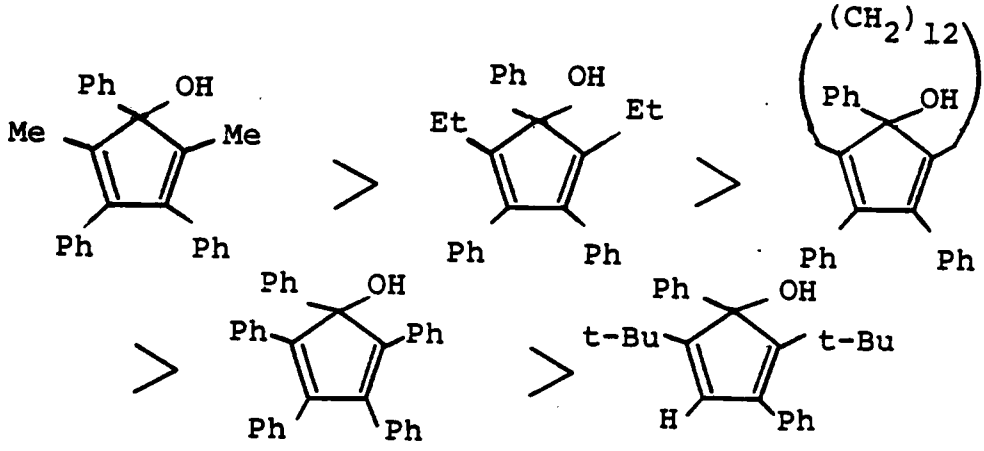




The relative rates for these compounds indicates that there are some major differences in these compounds.

The questions posed by this study were what difference would alkyl substituents make on the rates of the rearrangement relative to the parent case and does steric bulk at the migration terminus effect the rate of the rearrangement. The results for the relative rates indicate that the rearragements of these alcohols seem to differ with substituent. They do not indicate that the rearrangement is favored more when the alcohol has purely aromatic substituents than when the alcohol has some alkyl substituents. The results also do not indicate that there is a simple relation between steric bulk at the migration terminus and the rate of

rearrangement. A simple correlation of rate versus bulk would have yielded the following rate scheme.



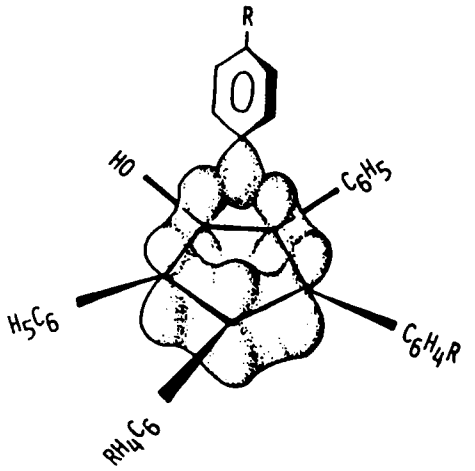
Although the di(t-butyl) alcohol had the slowest rate, and should have, the reason is unclear. Also, no explanation can be given for the fact that the cyclic alcohol is so fast and that the methyl, ethyl, and parent alcohols are so close together on the basis of bulk alone.

b. Thermodynamic Paramaters

The rearrangement of the cyclopentadienol system has been the subject of several kinetic studies.[3,5,7] Of interest in these studies was the elucidation of the reaction mechanism. Some studies had indicated that a linear free energy relation (LFER) was observed and, thus, the transition state would be partially charged.

Since the discovery by Youssef and Ogliaruso[3] that the rearrangement of the parent alcohol was not radical, was not affected by solvents of different dielectric constants, and

that it followed the Woodward and Hoffman rules, work has been undertaken to prove whether the mechanism is purely concerted or whether the transition state is charged. If the transition state was charged, a LFER would exist. Studies by Oldaker and Perfetti[7] indicated that a LFER did not exist in these systems. They proposed a purely concerted mechanism for this rearrangement as is shown here.



Transition state devoid of charge separation.

If one argued that the electronegative groups on the ring substituent were too far removed from the reaction to influence it, the previous results would not prove that a LFER did not exist. The current study investigated substituted alkyl groups of different size at the migration terminus. Since these groups are directly attached to the ring and are less electronegative than an aromatic ring, differ-

ences in the alkyl alcohols relative to the parent case would have introduced new questions into the study. The reaction rates and thermodynamic parameters for the alkyl alcohols compared to the parent case do not suggest a LFER.

The thermodynamic parameters are listed here in Table III and in the Appendix II.

Table III

Thermodynamic Parameters For All Alcohols

Compound (Alcohol)	Rate (170)	E_a	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
Parent	3.55×10^{-5}	31.0±1	30.0±1	-12.0±3
(Lit)[5]		35.0±1	34.1±1	-3.0±2
Cyclic	7.99×10^{-4}	32.0±2	31.0±2	- 3.0±5
Methyl	2.56×10^{-5}	32.0±2	31.0±2	-11.0±4
Ethyl	3.95×10^{-5}	29.0±1	28.0±1	-17.0±3

It is clear that the energy of activation and enthalpy of activation obtained for the parent alcohol are not very different from those obtained by Perfetti, and Oldaker[7] (given experimental errors). If energies of activation and enthalpy of activation for all of the alcohols of this study are considered, it is also clear that these values are the same, given experimental error. These observations are the same as those made by Perfetti and Oldaker, since they noticed little difference between the energies of activation and enthalpy of activation of the alcohols that they stu-

died. Both energies of activation and enthalpy of activation are dependent on the pathway of the reaction. Activation energy is a measure of the amount of energy needed to raise the energy of the reactant to the transition state level. Enthalpy of activation is a measure of the difference in bond energy of the reactant and the transition state. A series of compounds that undergo the same reaction and have similar energy of activation and enthalpy of activaton should react by similar mechanisms. The results that were obtained for enthalpy of activation and the energy of activation for the alcohols of this study support earlier theory that a LFER does not exist in these compounds and gives no proof that these rearrangements occur by any mechanism other than a purely concerted mechanism.

One does note by looking at Table III that there is a large difference between the rates for the cyclic alcohol and the others. The difference between these systems is due to the entropy of activation. Entropy of activation is independent of pathway[27] but reflects the difference in the degrees of freedom of vibrational, rotational, and translational states of the reactant and transition state.[28] An unfavorable entropy of activation means that a severe restriction has been placed on atoms in the transition state.[29]

In the systems that have been studied, the proposed mechanism requires the following restrictions. First, the

bent cyclopentadienol system must become planar. At the same time that this occurs, the migrating species must rotate to allow overlap of its orbitals with those of the ring system. The groups that are attached to the ring must move to a position that will not restrict the migration.

The cyclic alcohol is a strained molecule. The ring structure requires that this molecule have more order (less freedom) than the other studied alcohols. The cyclic structure of this alcohol restricts the ring flip that is common in these systems and thus slows its motion. The ring structure also holds the substituents in a rigid conformation (away from the migrating phenyl ring). The entropy of activation is thus more favorable, because the molecular order and structure of this alcohol are close to that of the transition state for the rearrangement.

If the entropies of activation for the parent, methyl, and ethyl alcohols are examined, it is readily seen why their entropies of activation are so much higher. The ground states of these molecules are less ordered than for the cyclic alcohol. The molecular ring flip occurs in these molecules and their substituents have relative freedom of motion and space. For these molecules to reach their transition state, a big increase in order is necessary and the entropy of activation is less favorable.

The entropies of activation of the methyl, ethyl, and parent alcohols are fairly close to each other. Few mean-

ingful observations can be made about the differences in these numbers. The fact that the entropy of activation for the methyl and parent alcohols are so very close is a reflection of the fact that the substituents at the 2- and 5-ring positions are single groups whose change in freedom in going to the transition state are equal. If any difference can be stated between these alcohols and the ethyl alcohol, it would be that the extra methyl group of the ethyl alcohol adds to the disorder of the ground state of the alcohol and creates a need for greater order in the transition state.

VI. Conclusions

The work presented here merits the following conclusions:

1. The condensation of benzil with 2,6-dimethyl-4-heptanone does not occur even when strong bases are used in the reaction. Steric hinderance to the condensation is postulated as the reason.
2. The synthesis of the 2,5-dialkyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ols can be accomplished by reacting either phenyllithium or phenylmagnesium bromide with the appropriate ketone. Phenyllithium is the better reagent because the yields and purity of the products of its reactions are superior to those of the phenylmagnesium bromide.
3. The thermal rearrangements of 2,5-dialkyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ols to ketones are possible. The rearrangement of the di(t-butyl) alcohol, which contained no 4-phenyl ring, was also possible.
4. Kinetic studies of the rearrangement of the alcohols indicated that the activation energy and enthalpy of activation for all alcohols rearrangements are essentially the same, suggesting that all of the alcohols rearranged by a similar mechanism.
5. The large difference in the rate of the rearrangement of the cyclic alcohol versus the parent alcohol is due to the difference in the entropy of activation.

Appendix I

Calculation of E_a, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$

A. 1,2,3,4,5-Pentaphenyl-2,4-cyclopentadien-1-ol

Temp °C	Temp °K	k Sec^{-1}	I/T $(^oK) \times 10^{-3}$	log k	log (k/T)
150	423	6.6×10^{-6}	2.36	-5.18	-7.81
160	433	1.73×10^{-5}	2.31	-4.74	-7.40
170	443	3.55×10^{-5}	2.26	-4.45	-7.1
185	458	1.19×10^{-4}	2.18	-3.92	-6.59
200	473	3.73×10^{-4}	2.11	-3.43	-6.10

E_a

for log k = $\frac{E_a}{RT}$ The Slope of log k vs $\frac{1}{T}$ = $\frac{E_a}{R(2.303)}$

E_a = (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

E_a = 31 Kcal/Mol

Y_{int} = 10.9

corr = -.996

$\Delta H^{\ddagger}$

for log $(\frac{k}{T})$ = $-\frac{\Delta H^{\ddagger}}{RT}$ the Slope of log $(\frac{k}{T})$ vs $\frac{1}{T}$ = $\frac{-\Delta H^{\ddagger}}{R(2.303)}$

$\Delta H^{\ddagger} = (-\text{Slope})(1.987)(2.303)$

Linear Least Squares Calculation

$\Delta H^{\ddagger} = 30$ Kcal/Mol

$Y_{int} = -7.85$

corr = -0.9995

$\Delta S^{\ddagger}$

$$\Delta S_1^{\ddagger}/4.576 = \log k - 10.753 - \text{Log } T + \frac{E_a}{4.576(T)}$$

$$\Delta S_1^{\ddagger} = 4.576\ [-4.45 - 10.753 - 2.65 + \frac{(31{,}050)}{4.576(443)}]$$

$$\Delta S_1^{\ddagger} = 4.576\ [-2.37]$$

$$\Delta S_1^{\ddagger} = -12 \text{ eu}$$

$$\Delta S_2^{\ddagger}/4.576 = Y_{int} - 10.32$$

$$\Delta S_2^{\ddagger} = 4.576(7.85 - 10.32)$$

$$\Delta S_2^{\ddagger} = -11 \text{ eu}$$

Continued

B. 15,16,17-Triphenylbicyclo[12.2.1]heptadeca-14,16-diene-17-ol

Temp °C	Temp °K	k Sec^{-1}	I/T $(^{o}K) \times 10^{-3}$	log k	log (k/T)
150	423	1.59×10^{-4}	2.36	-3.80	-6.42
160	433	3.9×10^{-4}	2.31	-3.46	-6.09
170	443	7.96×10^{-4}	2.26	-3.10	-5.75

E_a

for log k = $\frac{E_a}{RT}$ The Slope of log k vs $\frac{1}{T}$ = $\frac{E_a}{R(2.303)}$

E_a = (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

E_a = 32.0 Kcal/Mol

Y_{int} = 12.72

Corr = -1

$\Delta H^{\ddagger}$

for log $(\frac{k}{T})$ = $-\frac{\Delta H^{\ddagger}}{RT}$ the Slope of log $(\frac{k}{T})$ vs $\frac{1}{T}$ = $\frac{-\Delta H^{\ddagger}}{R(2.303)}$

$\Delta H^{\ddagger}$ = (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

$\Delta H^{\ddagger}$ = 31 Kcal/Mol

Y_{int} = 9.39

Corr = -0.9999

$\Delta S^{\ddagger}$

$$\Delta S_1^{\ddagger}/4.576 = \log k - 10.753 - \text{Log } T + \frac{E_a}{4.576(T)}$$

$$\Delta S_1^{\ddagger} = 4.576\ [-3.10 - 10.753 - 2.65 + \frac{(32,000)}{4.576(443)}]$$

$$\Delta S_1^{\ddagger} = 4.576\ [-0.717]$$

$$\Delta S_1^{\ddagger} = -3 \text{ eu}$$

$$\Delta S_2^{\ddagger}/4.576 = (Y_{int} - 10.32)$$

$$\Delta S_2^{\ddagger} = 4.576(9.39 - 10.32)$$

$$\Delta S_2^{\ddagger} = -4 \text{ eu}$$

Continued

C. 2,5-Diethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

Temp °C	Temp °K	k Sec^{-1}	I/T (^{o}K) X 10^{-3}	log k	log (k/T)
170	443	3.95 X 10^{-5}	2.26	-4.40	-7.05
185	458	1.18 X 10^{-4}	2.18	-3.93	-6.59
200	473	3.5 X 10^{-4}	2.11	-3.46	-6.13

E_a

for log k = $\frac{E_a}{RT}$ The Slope of log k vs $\frac{1}{T}$ = $\frac{E_a}{R(2.303)}$

E_a = (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

E_a = 29 Kcal/Mol

Y_{int} = 9.73

Corr = -0.999

$\Delta H^{\ddagger}$

for log $(\frac{k}{T})$ = $-\frac{\Delta H^{\ddagger}}{RT}$ the Slope of log $(\frac{k}{T})$ vs $\frac{I}{T}$ = $\frac{-\Delta H^{\ddagger}}{R(2.303)}$

$\Delta H^{\ddagger}$= (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

$\Delta H^{\ddagger}$= 28 Kcal/Mol

$Y_{int} = 6.78$

Corr = -0.999

$\Delta S^{\ddagger}$

$$\Delta S_1^{\ddagger}/4.576 = \log k - 10.753 - \text{Log } T + \frac{E_a}{4.576(T)}$$

$$\Delta S_1^{\ddagger} = 4.576\ [-4.40 - 10.753 - 2.65 + \frac{(28,630)}{4.576(443)}]$$

$$\Delta S_1^{\ddagger} = 4.576\ [3.683]$$

$$\Delta S_1^{\ddagger} = -17 \text{ eu}$$

$$\Delta S_2^{\ddagger}/4.576 = Y_{int} - 10.32$$

$$\Delta S_2^{\ddagger} = 4.576(6.78 - 10.32)$$

$$\Delta S_2^{\ddagger} = -16 \text{ eu}$$

Continued

D. 2,5-Dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

Temp °C	Temp °K	k Sec^{-1}	I/T $(^{o}K) \times 10^{-3}$	log k	log (k/T)
170	443	2.58×10^{-5}	2.26	-4.59	-7.24
185	458	9.7×10^{-5}	2.18	-4.01	-6.67
200	473	2.77×10^{-4}	2.11	-3.56	-6.23

E_a

for $\log k = \frac{E_a}{RT}$ The Slope of log K vs $\frac{1}{T} = \frac{E_a}{R(2.303)}$

Ea = (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

E_a = 32 Kcal/Mol

Y_{int} = 10.96

Corr = -0.999

$\Delta H^{\ddagger}$

for $\log (\frac{k}{T}) = -\frac{\Delta H^{\ddagger}}{RT}$ the Slope of $\log (\frac{k}{T})$ vs $\frac{I}{T} = \frac{-\Delta H^{\ddagger}}{R(2.303)}$

$\Delta H^{\ddagger}$ = (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

$\Delta H^{\ddagger}$ = 31 Kcal/Mol

Y_{int} = 8.01

Corr =-0.999

$\Delta S^{\ddagger}$

$$\Delta S_1^{\ddagger}/4.576 = \log k - 10.753 - \text{Log } T + \frac{E_a}{4.576(T)}$$

$$\Delta S_1^{\ddagger} = 4.576\ [-4.59 - 10.753 - 2.65 + \frac{(31,460)}{4.576(443)}]$$

$$\Delta S_1^{\ddagger} = -11 \text{ eu}$$

$$\Delta S_2^{\ddagger}/(2.30)(R) = Y_{int} - 10.32$$

$$\Delta S_2^{\ddagger} = 4.576[8.01 - 10.32]$$

$$\Delta S_2^{\ddagger} = -11 \text{ eu}$$

Continued

E. 2,5-Dimethyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ol

Temp °C	Temp °K	k Sec^{-1}	I/T (^{o}K) X 10^{-3}	log k	log (k/T)
170	443	1.45 X 10^{-5}	2.26	-4.84	-7.49
185	458	5.4 X 10^{-5}	2.18	-4.27	-6.93
200	473	1.77 X 10^{-4}	2.11	-3.75	-6.43

E_a

for log k = $\frac{E_a}{RT}$ The Slope of log K vs $\frac{1}{T}$ = $\frac{E_a}{R(2.303)}$

E_a = (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

E_a = 33 Kcal/Mol

Y_{int} = 11.6

Corr = -0.999

$\Delta H^{\ddagger}$

for log $(\frac{k}{T})$ = $-\frac{\Delta H^{\ddagger}}{RT}$ the Slope of log $(\frac{k}{T})$ vs $\frac{I}{T}$ = $\frac{-\Delta H^{\ddagger}}{R(2.303)}$

$\Delta H^{\ddagger}$ = (-Slope)(1.987)(2.303)

Linear Least Squares Calculation

$\Delta H^{\ddagger}$ = 32 Kcal/Mol

Y_{int} = 8.48

Corr = -0.999

$\Delta S^{\ddagger}$

$$\Delta S_1^{\ddagger}/4.576 = \log k - 10.753 - \text{Log } T + \frac{E_a}{4.576(T)}$$

$$\Delta S_1^{\ddagger} = 4.576\ [-4.84 - 10.753 - 2.65 + \frac{(33,200)}{4.576(443)}]$$

$$4.576[-1.86]$$

$$\Delta S_1^{\ddagger} = -9 \text{ eu}$$

$$\Delta S_2^{\ddagger} = 4.576[Y_{int} - 10.32]$$

$$\Delta S_2^{\ddagger} = 4.576[8.48 - 10.32]$$

$$\Delta S_2^{\ddagger} = -8 \text{ eu}$$

Appendix II

Summary of Calculations for E_a, $\Delta H^{\ddagger}$ $\Delta S_1^{\ddagger}$, $\Delta S_2^{\ddagger}$

Alcohol	E_a(Kcal)	$\Delta H^{\ddagger}$(Kcal)	$\Delta S_1^{\ddagger}$ (eu)	$\Delta S_2^{\ddagger}$ (eu)
Parent	31.0±1.1	30.0±1.0	-12.0±3.0	-11.0±3.0
Ethyl	29.0±1.0	28.0±1.0	-17.0±3.0	-16.0±3.0
Methyl	32.0±2.0	31.0±2.0	-11.0±4.0	-11.0_4.0
Cyclic	32.0±2.0	31.0±2.0	- 3.0±5.0	- 4.0±5.0

Appendix III

LC Parameters For The Alcohols and Ketones

a. Micro Pac NH_2-10 30cm X 4mm column

Alcohol	Solvent (%)		Flow Rate	Retention time (min)	
	Hexane	Methanol	ml/min	Alcohol	Ketones
Parent	99.0	1.0	1.3	9	4
Cyclic	99.9	0.1	1.7	6	15.4
Methyl	99.25	0.75	1.7	8.5	12
Ethyl	99.5	0.5	1.7	5.8	10.4

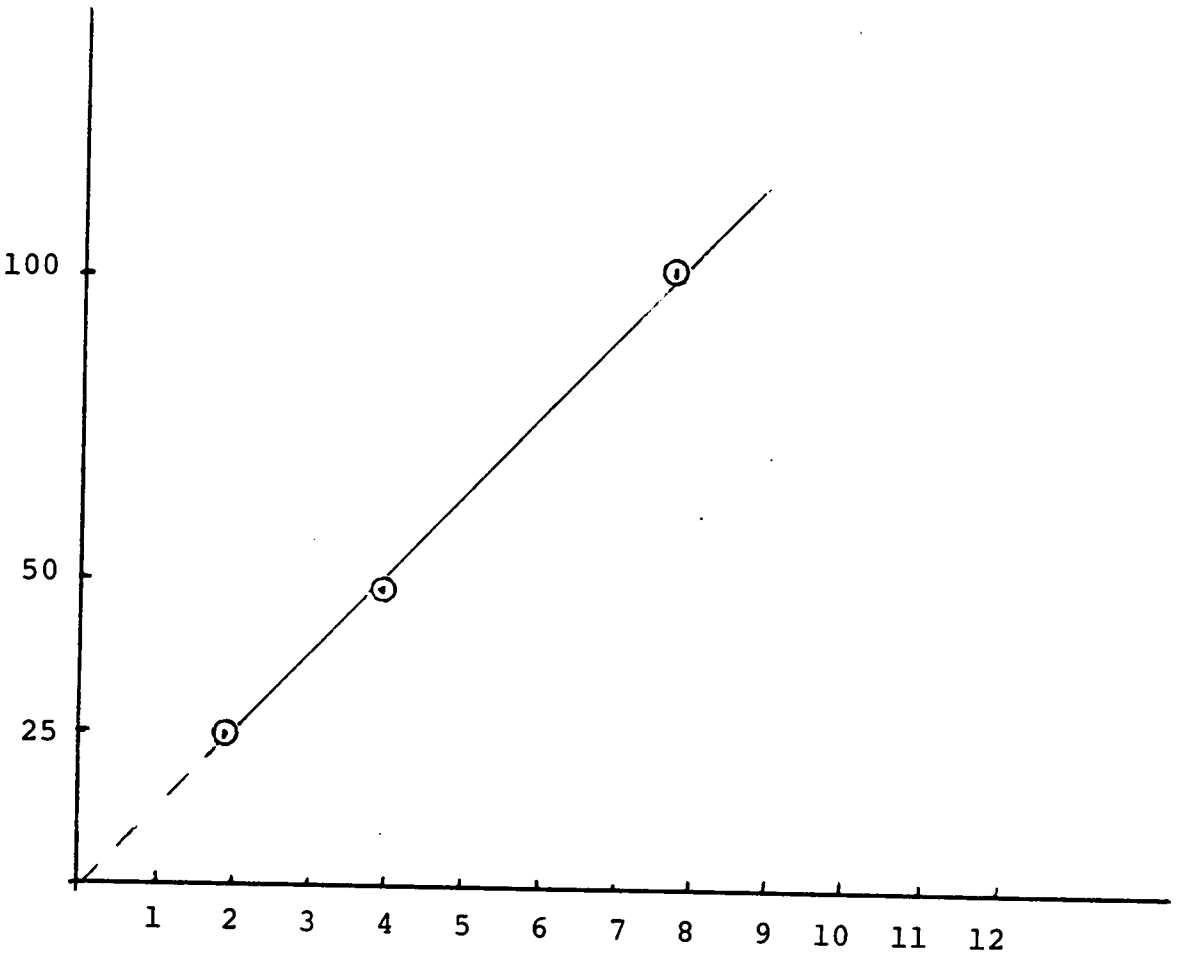
b. Silica gel column Woelum 10μ Silica 2.5 cm X 3 mm column

Alcohol	Solvent (%)		Flow Rate	Retention time (min)	
	Hexane	Methanol	ml/min	Alcohol	Ketones
Parent	99.9	0.1	1.3	6.6	3.6
Cyclic	99.9	0.1	1.3	5.4	2.8
Methyl	100.0	0.0	1.3	14.0	2.2
Ethyl	99.9	0.1	1.3	14.2	2.8

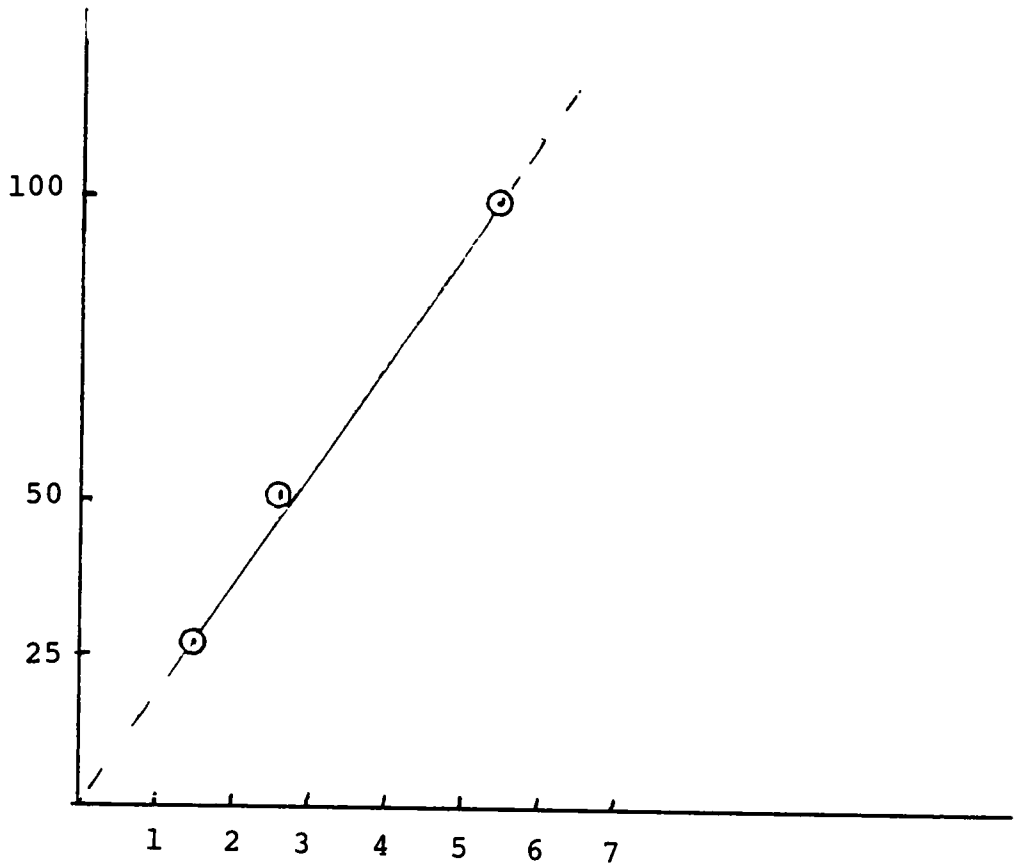
Appendix IV

Calibration Curves For All Alcohols

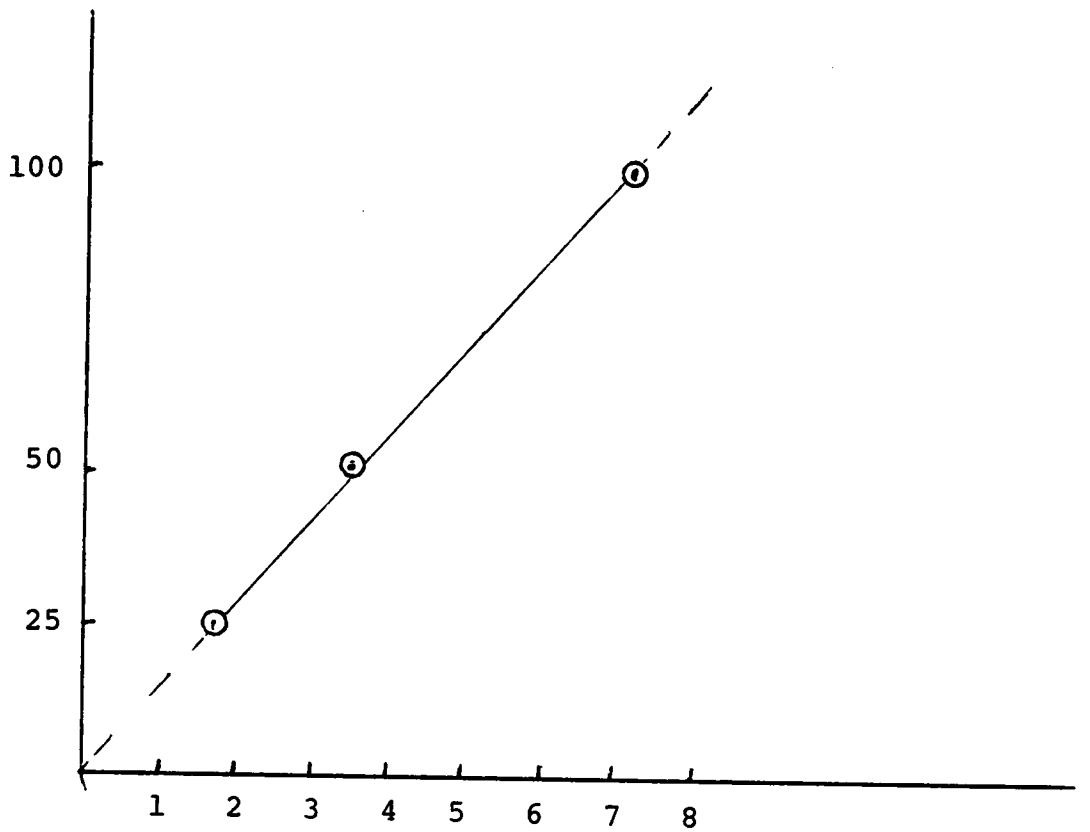
a. Parent [% Alcohol versus Area (cm^2)]



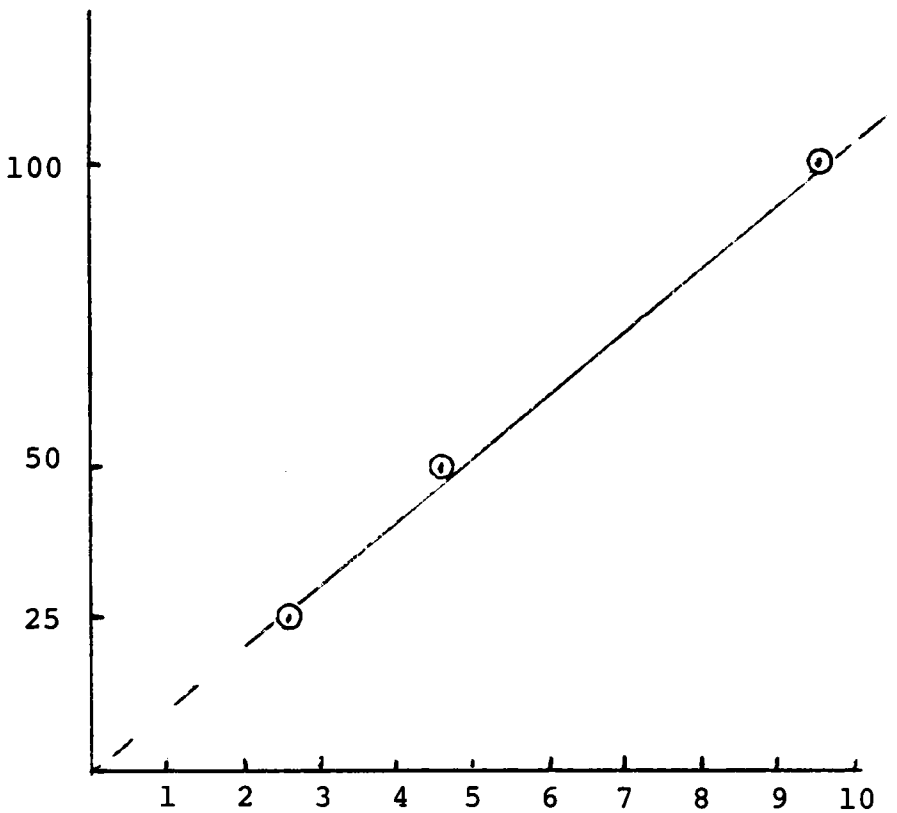
b. Ethyl [% Alcohol versus Area (cm^2)]



c. Cyclic [% Alcohol versus Area (cm^2)]



d. Methyl [% Alcohol versus Area (cm^2)]



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THE SYNTHESIS AND THERMAL REARRANGEMENT OF 2,5-DIALKYL-1,3,4-TRIPHENYL-2,4-CYCLOPENTADIEN-1-OL'S

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(ABSTRACT)

Three 2,5-dialkyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ols and 2,5-di(t-butyl)-1,3-diphenyl-2,4-cyclopentadien-1-ol were prepared from their precursor ketones using phenyllithium and Grignard reagent. In general, the phenyllithium reagent produced products faster and in better yield and purity than did the Grignard reagent. The alcohols were rearranged thermally to obtain the appropriate ketones and to obtain information about the relative rates of the rearrangement. The rearrangement of the three 2,5-dialkyl-1,3,4-triphenyl-2,4-cyclopentadien-1-ols were studied kinetically and the results compared with those obtained from similar studies on 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol. The alcohols all possessed energies of activation and enthalpies of activation which were essentially identical, these supporting earlier theory that no linear free energy relationship (LFER) exists in these rearrangements and that a purely concerted mechanism exists in these cases. The

rate of reaction for 15,16,17-triphenylbicyclo[12.2.1] heptadeca-14,16-dien-1-ol was very much faster than any other studied alcohol. The difference in this rate is thought to be due to the severe steric restraints that are present in this alcohol. The entropy of activation for this strained alcohol was shown to be much less than for the other alcohols.